PROCEEDINGS

OF

THE CHEMICAL SOCIETY.

Vol. XXIV. Nos. 335—349.

JANUARY—DECEMBER, 1908.

LONDON:
GURNEY & JACKSON, 10, PATERNOSTER ROW.
1909.

RICHARD CLAY AND SONS, LIMITED,
BREAD STREET HILL, E.C., AND
BUNGAY, SUFFOLK.

540.G C42 v. 24-26

LIST OF GRANTS MADE FROM THE RESEARCH FUND DURING THE YEAR 1908.

£18 to H. Bassett, jun.: formation of tricalcium and tetracalcium phosphates.

£15 to G. D. Bengough: measurement of the rate of change in solid alloys.

£10 to J. C. Cain: preparation of substituted nitrosoacetylamino-compounds of the aromatic series. Constitution of santalin.

£10 to R. M. Caven and H. J. S. Sand: determination of the decomposition-temperature curves of the alkali bicarbonates.

£15 to F. D. Chattaway: action of halogens on urea, substituted ureas, and guanidine.

£5 to A. Clayton: preparation and constitution of coumarinic acid.

£5 to J. B. Cohen: relation of position isomerism to optical activity.

£5 to C. H. Desch: process of diffusion in solid solutions.

£5 to A. E. Dunstan: relation between viscosity and chemical constitution (continued).

£7 to K. Fisher: constitution of alkaloid cryptopin.

£5 to J. A. N. Friend: action of steam on red-hot iron.

£5 to N. L. Gebhard: reactions of hydroxylamines and aromatic diazo-compounds.

£20 to C. Gilling: hydroaromatic ketones.

£20 to A. G. Green: constitution of synthetic colouring matters (continued).

£7 to P. Haas: dimethyldihydroresorcin, and its nitrogen derivatives (continued).

£5 to H. B. Hartley: preparation of "pure water," and determination of the conductivity of dilute solutions of acids in it.

£7 to W. N. Haworth: condensations with ethyl cyanoacetate (continued).

£5 to G. S. Hibbert: reduction of hydroxy-ortho-toluic acid.

£10 to T. P. Hilditch: influence of unsaturated groups in the molecule on the rotatory power of optically active compounds.

£5 to Miss A. Homer: preparation of dinaphthanthracene. The action of aluminium chloride on benzene and toluene.

£5 to E. Hope: condensations with ethyl β-bromomethylmalonate.

£10 to T. M. Lowry: studies in dynamic isomerism (continued).

£10 to A. McKenzie: investigation of the Walden inversion.

£7 to A. N. Meldrum: reduction of hydroxy-meta-toluic acid (continued).

£10 to G. T. Morgan: influence of substitution on the tinctorial properties of azo-dyes and allied colouring matters.

£10 to T. S. Patterson: rotation of active compounds of aliphatic nitro-derivatives. Isomerism in the thiocyanates and *iso*thiocyanates.

£5 to W. H. Patterson: nature of occluded hydrogen.

£8 to F. M. Perkin: electrolytic and other oxidations of organic compounds. Condensations by means of calcium ethoxide.

£10 to R. H. Pickard and J. Yates: constitution of cholesterol (continued).

£5 to R. H. Pickard: isomerides of natural *l*-menthol.

£5 to F. G. Pope: relation between colour and constitution in the azomethine series.

£8 to T. S. Price: preparation of disulphides and diselenides (continued).

£5 to S. M. Revington and I. G. Rankin: sulphides and oxysulphides of silicon.

£10 to R. Robinson: synthesis of papaverine; and investigation of pyranol salts.

£10 to J. L. Simonsen: formation and properties of the *cyclo*butane ring. Attempt to synthesise norpinic acid. Action of chloromethyl ether on ethyl acetoacetate (continued).

£10 to Miss I. Smedley: refractive indices of unsaturated compounds.

£10 to S. Smiles: some thio-compounds.

£5 to R. Storey: resolution of methyltetrahydrobenzoic acid into its optically active modifications.

£10 to J. J. Sudborough: "Steric Hindrance," and polynitro-compounds (continued).

£10 to W. B. Tuck: absorption spectra of nitrosophenols and nitrosonaphthols, and of substituted azo-compounds. The relation of absorption spectra of nitrophenols.

£3 to C. H. Warner: investigation of nitrophthalic acids.

£8 to H. Wren: preparation of optically active ketols and their derivatives.

£10 to G. Young: heterocyclic compounds (continued).

Total amount granted during 1908 = £368.

LIST OF FELLOWS ELECTED DURING 1908.

Name.	Proposed.	Elected.
Akers, Noel Charles	October 22nd, 1908	December 3rd.
Allen, Thomas Boles	November 19th, 1908.	,, ,,
Allmand, Arthur John	February 6th, 1908	May 7th.
Andreae, Edward Philip	December 5th, 1907.	February 20th.
Aubertin, Thomas	June 4th, 1908	December 3rd.
Ba, Maung	November 19th, 1908.	,, ,,
Baker, Thomas James	November 5th, 1908.	,, ,,
Baker, William Henry Benson	February 6th, 1908	May 7th.
Ballantyne, William Henry	May 21st, 1908	June 18th.
Barr, Guy	December 19th, 1907.	February 20th.
Barrett, Maurice	October 22nd, 1908	December 3rd.
Barton, Robert, jun.	January 16th, 1908	February 20th.
Bevan, Edward Morris	May 21st, 1908	June 18th.
Bhunsri, Prince Mom Chow	November 19th, 1908.	December 3rd.
Bickerstaffe, Robert	October 22nd, 1908	,, ,,
Birch, William Colet	June 18th, 1908	,, ,,
Blyther, Donald Francis	April 2nd, 1908	June 18th.
Bowen, Josiah Leonard	February 6th, 1908	May 7th.
Brakes, William Sudderick	October 22nd, 1908	December 3rd.
Braun, Marie Joseph Arsène	December 5th, 1907.	February 20th.
Brown, Harry James	January 16th, 1908	,, ,,
Brown, James	May 21st, 1908	June 18th.
Brown, Walter, jun.	December 19th, 1907.	February 20th.
Carpenter, John Arthur	November 21st, 1907.	February 20th.
Clarke, Hans Thacher	January 16th, 1908	,, ,,
Clement, Leonard	October 22nd, 1908	December 3rd.
Collens, Archibald Edgar	December 19th, 1907.	February 20th.
Collier, William Henry	December 5th, 1907.	,, ,,
Cooper, Charles Duncan	May 7th, 1908	June 18th.
Coverdale, Arthur Edward	March 5th, 1908	May 7th.
Cowburn, John Robert	May 7th, 1908	June 18th.
Cowley, Robert Charles	October 22nd, 1908	December 3rd.
Crichton, David Cowan	December 19th, 1907.	February 20th.
Dickinson, Cyril	November 21st, 1907.	,, ,,
Duckworth, Hugh Cecil	October 22nd, 1908	December 3rd.
Dunnicliff, Horace Barratt	,, ,, ,,	,, ,,
Dutt, Bidhu Bhushan	February 20th, 1908	May 7th.
Eagles, Edwin Mortimer	November 21st, 1907.	February 20th.
Easton, Reginald Freeman	October 22nd, 1908	December 3rd.
Everitt, Charles	November 5th, 1908.	,, ,,
Fairburn, Henry	October 22nd, 1908	,, ,,
Fairweather, James Hill	May 21st, 1908	June 18th.

Name.	Proposed.	Elected.
Falk, Kaufman George	May 7th, 1908	June 18th.
Findley, Albert Edward	February 20th, 1908	May 7th.
Francies, Joseph Valentine	January 16th, 1908	February 20th.
Gale, Robert Cecil	November 21st, 1907.	,, ,,
Gānguli, Atul Chandra	February 20th, 1907	May 7th.
Gilling, Charles	February 6th, 1908	,, ,,
Girvan, Arthur Frank	October 22nd, 1908	December 3rd.
Green, Henry Hamilton	November 5th, 1908.	,, ,,
Green, Leonard Clifford	March 19th, 1908	May 7th.
Griffin, John	June 18th, 1908	December 3rd.
Hall, William	March 19th, 1908	May 7th.
Hebron, John Henry Albert	October 22nd, 1908	December 3rd.
Heron, John Maxwell	December 5th, 1907	February 20th.
Hilditch, Thomas Percy	,, ,, ,,	,, ,,
Hinds, Cyril Arden	April 2nd, 1908	May 7th.
Hinks, Edward	November 5th, 1908.	December 3rd.
Holden, George Edward	February 20th, 1908	May 7th.
Holland, Frank William Crossley	May 21st, 1908	June 18th.
Holland, Norman	May 7th, 1908	,, ,,
Hornby, Percy Holme	February 20th, 1908	May 7th.
Horrobin, Arthur	,, ,, ,,	,, ,,
Hughes, Joseph Albert	June 18th, 1908	December 3rd.
Hull, Thomas Ernest	,, ,, ,,	,, ,,
Hutchinson, Henry Brougham	April 2nd, 1908	June 18th.
Irvine, James Colquhoun	June 18th, 1908	December 3rd.
Johnson, Grove	October 22nd, 1908	,, ,,
Keiller, Patrick Anderson	,, ,, ,,	,, ,,
Kenyon, Joseph	November 5th, 1908.	,, ,,
King, James Kirkman	May 7th, 1908	June 18th.
Kohn, Hugo Stefan	March 19th, 1908	May 7th.
Krishnayya, H. V.	June 18th, 1908	December 3rd.
Larmuth, Lionel Gordon	May 7th, 1908	June 18th.
Linch, Frank William	October 22nd, 1908	December 3rd.
Lindley, Arthur Stanley	,, ,, ,,	,, ,,
Lyell, Henry Robert	May 7th, 1908	June 18th.
Lynch, Gerald Roche	March 19th, 1908	May 7th.
MacGregor, Gregor	November 5th, 1908.	December 3rd.
Mansfield, Herbert	February 20th, 1908.	May 7th.
Maywald, Frederick J.	March 5th, 1908	,, ,,
Meade, Alwyne Harcourt	February 6th, 1908	,, ,,
Meggitt, Alfred Ash	May 21st, 1908	June 18th.
Melling, Samuel Ernest	March 5th, 1908	May 7th.
Menzies, Frederick Martin Kay	June 18th, 1908	December 3rd.
Merrick, Arnold	January 16th, 1908	February 20th.
Miles, William Herbert	November 5th, 1908.	December 3rd.
Millar, Charles James	,, ,, ,,	,, ,,
Minett, Edward Pigott	October 22nd, 1908	,, ,,
Morgan, Howard Houlston	June 18th, 1908	,, ,,
Morewood, Capel Darcy	December 5th, 1907	February 20th.

Name.	Proposed.	Elected.
Neech, Herbert Richard	February 6th, 1908...	May 7th.
Neogi, Panchānan	February 20th, 1908..	,, ,,
Norman, Cyril Lawrence	October 22nd, 1908...	December 3rd.
Normand, Alexander Robert	,, ,, ,,	,, ,,
Oke, Alfred William	December 5th, 1907..	February 20th.
Okell, Stanley Allen Warrington	April 2nd, 1908	June 18th.
Pearson, George Edward	November 5th, 1908.	December 3rd.
Pearson, John William	June 4th, 1908	,, ,,
Perry, Frank	,, ,, ,,	,, ,,
Phillips, Thomas Richards	February 6th, 1908...	May 7th.
Pingriff, George Neville	November 21st, 1907.	February 20th.
Pinnock, Douglas Robert	December 5th, 1907..	,, ,,
Power, George O'Brien	June 4th, 1908	December 3rd.
Ray, Haradhan	May 7th, 1908	June 18th.
Readwin, William	,, ,, ,,	,, ,,
Rennie, Alexander	October 22nd, 1908...	December 3rd.
Rhead, Ezra Lobb	,, ,, ,,	,, ,,
Richards, Francis Edward	February 6th, 1908...	May 7th.
Roach, William Frothingham	June 4th, 1908	December 3rd.
Runeckles, Arthur Robert	December 5th, 1907..	February 20th.
Rutter, Clement Thomas	May 21st, 1908	June 18th.
Salamon, Maurice Salamon	October 22nd, 1908 ..	December 3rd.
San, Maung U.	November 19th, 1908	,, ,,
Saunderson, William	October 22nd, 1908...	,, ,,
Scott, Andrew L.	December 19th, 1907.	February 20th.
Seelhorst, William	April 2nd, 1908	May 7th.
Shaw, William Bayliss	November 21st, 1907.	February 20th.
Shilstone, Herbert M.	November 19th, 1908.	December 3rd.
Singh, Puran	December 19th, 1907.	February 20th.
Smythe, John Armstrong	,, ,, ,,	,, ,,
Sommerfeldt, Ernst	October 22nd, 1908..	December 3rd.
Southcombe, James Edward	May 21st, 1908	June 18th.
Speed, John Day	April 2nd, 1908 ...	,, ,,
Spiers, Charles Sedgley	December 19th, 1907.	February 20th.
Stead, Arthur	January 16th, 1908...	,, ,,
Stewart, Alexander Mackintosh	May 7th, 1908	June 18th.
Stokes, Edward	May 21st, 1908	,, ,,
Tate, Francis George Henry	October 22nd, 1908..	December 3rd.
Thomas, Frank Moreton	November 5th, 1908.	,, ,,
Trechmann, Adolph Octavius	December 5th, 1907..	February 20th.
Tyson, Thomas Marshall	January 16th, 1908...	,, ,,
Unwin, Harry Jackson	November 21st, 1907.	,, ,,
Vidyant, Hari Prasad	May 21st, 1908 ...	June 18th
Wade, Alfred	December 5th, 1907..	February 20th.
Walker, Herbert	November 21st, 1907.	,, ,,
Walton, Sidney Gilbert	November 5th, 1908.	December 3rd.
Ward, Herbert Horace	May 7th, 1908	June 18th.
Watkins, Edwin John	March 5th, 1908	May 7th.

Name.	Proposed.	Elected.
Watson, Herbert Edmeston	December 5th, 1907..	February 20th.
Watson, John	December 19th, 1907.	,, ,,
Watt, John	November 19th, 1908.	December 3rd.
Watt, Robert Dickie	October 22nd, 1908...	,, ,,
Weighell, Arthur	,, ,, ,,	,, ,,
Wheatley, William	February 6th, 1908...	May 7th.
Williams, David Thomas	January 16th, 1908...	February 20th.
Williams, Joseph Henry	November 21st, 1907.	,, ,,
Williams, Frederick	October 22nd, 1908..	December 3rd.
Wilson, Harry Percy	December 5th, 1907..	February 20th.
Winterson, William George	October 22nd, 1908...	December 3rd.
Withey, William Henry	December 19th, 1907.	February 20th.
Wood, Francis Charles Benjamin	January 16th, 1908...	,, ,,
Wootton, William Ord	November 5th, 1908.	December 3rd.
Worley, Frederick Palliser	,, ,, ,,	,, ,,
Wright, Allister MacLean	October 22nd, 1908...	,, ,,
Wright, Charles Harold	May 7th, 1908	June 18th.
Yates, Harry James	May 21st, 1908	,, ,,
Yates, Joseph	December 19th, 1907.	February 20th.
Young, Charles Robert	May 7th, 1908	June 18th.

HONORARY AND FOREIGN MEMBERS ELECTED DURING 1908.

Name.	Proposed.	Elected.
Le Bel, Joseph Achille	January 16th, 1908...	February 6th.
Le Chatelier, Henry Louis	,, ,, ,,	,, ,,
Gautier, Armand Emile Justin	,, ,, ,,	,, ,,
Haller, Albin	,, ,, ,,	,, ,,
Hittorf, Johann Wilhelm	,, ,, ,,	,, ,,
Richards, Theodore William	,, ,, ,,	,, ,,
Wallach, Otto	,, ,, ,,	,, ,,

FELLOWS DECEASED, 1908.

Name.	Elected.	Died.
Ball, James Handby	June 18th, 1902	September 10th, 1908.
Banner, Samuel	February 2nd, 1888	January 11th, 1908.
*Becquerel, Antoine Henri	May 18th, 1904	August 25th, 1908.
Brough, Bennett Hooper	January 17th, 1884	October 3rd, 1908.
Cart, John Trevor	February 21st, 1907	September 5th, 1908.
Cunnington, Alfred Valentine	December 1st, 1898	October 8th, 1908.
Deck, Arthur	December 3rd, 1874	September 3rd, 1908.
Evans, Sir John	June 16th, 1876	May 31st, 1908.
Fasnacht, Eugène Arthur	February 19th, 1902	February 1st, 1908.
Friswell, Richard John	February 2nd, 1871	February 6th, 1908.
Gamble, Sir Josias Christopher	April 6th, 1876	September 24th, 1908.
Gerard, Thomas Alfred	June 15th, 1904	June 14th, 1907.
*Gibbs, Wolcott	May 3rd, 1866	December 9th, 1908.
Habirshaw, William Martin	June 4th, 1874	
Harland, Robert Henry	June 1st, 1876	November 25th, 1908.
Hart, Frederick William	January 21st, 1869	March 13th, 1908.
Helms, Albert	December 6th, 1894	May 28th, 1907.
Houldershaw, Arthur	February 7th, 1901	May 2nd, 1908.
Jackson, Raynsford Valentine	December 15th, 1881	November 3rd, 1908.
Johnson, John Grove	May 16th, 1872	March 18th, 1908.
Jowett, William Hall	February 21st, 1891	September 23rd, 1908.
Leeds, Frank Henley	June 18th, 1891	April 30th, 1908.
Morson, Thomas	December 15th, 1851	February 5th, 1908.
Pendlebury, Harold Lawson	July 5th, 1907	March 31st, 1908.
Player, Jacob Hort	November 15th, 1860	February 24th, 1908.
Shenstone, William Arthur	February 17th, 1876	February 3rd, 1908.
Sibson, Alfred	December 15th, 1859	December 31st, 1908.
Smith, Frank Gurney	December 3rd, 1903	February 17th, 1908.
Sonstadt, Edward	December 17th, 1874	July 5th, 1908.
Stevenson, Sir Thomas	February 18th, 1864	July 27th, 1908.
Thwaite, Benjamin Howarth	December 2nd, 1880	May 2nd, 1908.
Wade, Alfred	February 20th, 1908	March 17th, 1908.
Walker, Thomas Hatfield	April 17th, 1879	February 27th, 1907.

* Honorary and Foreign Member.

TITLES OF PAPERS COMMUNICATED TO THE SOCIETY DURING 1908.

	Page in Proceedings.	Page in Transactions.
January 16th.		
1. Colour and constitution of azo-compounds. Part II. The salts of *p*-hydroxyazo-compounds with mineral acids. By John Jacob Fox and John Theodore Hewitt	6	333
2. A new method of determining vapour densities. Part I. By Philip Blackman	8	—
3. Studies in the camphane series. Part XXV. Action of diazomethane on the two modifications of *iso*-nitrosocamphor. By Martin Onslow Forster and Henry Holmes	8	242
4. The oxidation of aromatic hydrazines by metallic oxides, permanganates, and chromates. By Frederick Daniel Chattaway	10	270
5. Studies in fermentation. Part II. The mechanism of alcoholic fermentation. By Arthur Slator	11	217
6. Organic derivatives of silicon. Part IV. The sulphonation of benzylethylpropylsilicyl oxide and of benzylethyldipropylsilicane. By Herbert Marsden and Frederic Stanley Kipping	12	198
7. The formation and reactions of imino-compounds. Part VI. The formation of derivatives of hydrindene from *o*-phenylenediacetonitrile. By Charles Watson Moore and Jocelyn Field Thorpe	12	165
8. Valency. By John Albert Newton Friend	14	260
9. The esterification constants of the normal fatty acids. By John Joseph Sudborough and James Mylam Gittins	14	210
10. The anomalous behaviour of the hydrogen electrode in solutions of lead salts and the existence of univalent lead ions in aqueous solutions. By Henry George Denham and Arthur John Allmand	14	424
11. Amphoteric metallic hydroxides. Part I. By John Kerfoot Wood	15	411
12. The use of pyridine bases as halogen carriers. By William Ernest Cross and Julius Berend Cohen	15	—
13. Decomposition of hyponitrous acid. By Edward Divers	16	—
February 6th.		
14. The metallic picrates. By Oswald Silberrad and Henry Ablett Phillips	22	474

	Page in Proceedings.	Page in Transactions.
15. Some physico-chemical properties of mixtures of pyridine and water. By Harold Hartley, Noel Garrod Thomas, and Malcolm Percival Applebey.....	22	538
16. The constitution of umbellulone. Part III. By Frank Tutin	23	252
17. Colour and constitution of azomethine compounds. Part I. By Frank George Pope.....	24	532
18. The preparation of *l*-benzoin. By Alexander McKenzie and Henry Wren	25	309
19. Organic derivatives of silicon. Part V. Benzylethylsilicone, dibenzylsilicone, and other benzyl and benzylethyl derivatives of silicane. By Robert Robison and Frederic Stanley Kipping	25	439
20. The residual affinity of the coumarins and thiocoumarins as shown by their additive compounds. By Arthur Clayton	26	524
21. The influence of foreign substances on certain transition temperatures and the determination of molecular weights. By Harry Medforth Dawson and Colin Gyrth Jackson	26	344
22. The bromination of *p*-hydroxydiphenylamine. By Alice Emily Smith and Kennedy Joseph Previté Orton	27	314
23. The decomposition of ammonium dichromate by heat. By William Marrs Hooton	27	—
24. The effect of constitution on the rotatory power of optically active nitrogen compounds. Part II. By Humphrey Owen Jones and John Robertshaw Hill...	28	295
25. Malacone, a silicate of zirconium. By Alexander Charles Cumming	28	350
26. The reducibility of magnesium oxide by carbon. By Roland Edgar Slade	29	327
27. The crystal form of halogen derivatives of open-chain hydrocarbons with reference to the Barlow-Pope theory of structure. By Frans Maurits Jaeger.....	29	517
28. The determination of the rate of chemical change by measurement of the gases evolved. By Francis Edward Everard Lamplough	29	—
29. The temperatures of spontaneous crystallisation of mixed solutions, and their determination by means of the index of refraction. Mixtures of solutions of sodium nitrate and lead nitrate. By Florence Isaac.	30	384
30. Contributions to the chemistry of the terpenes. Part III. Some oxidation products of pinene. By George Gerald Henderson and Isidore Morris Heilbron	31	288
31. A β-lactonic acid from acetone and malonic acid. By Andrew Norman Meldrum	31	598
February 20th.		
32. Organic derivatives of silicon. Part VI. The optically active sulphobenzylethylpropylsilicyl oxides. By Frederic Stanley Kipping	47	457

	Page in Proceedings.	Page in Transactions.
33. The preparation of conductivity water. By Harold Hartley, Norman Phillips Campbell, and Reginald Holliday Poole	47	428
34. Derivatives of para-diazoiminobenzene. By Gilbert Thomas Morgan and Frances Mary Gore Mickle-thwait	48	602
35. The affinity constants of bases as determined by the aid of methyl-orange. By Victor Herbert Veley	50	652
36. The action of thionyl chloride and of phosphorus pentachloride on the methylene ethers of catechol derivatives. By George Barger	50	563
37. A study of the diazo-reaction in the diphenyl series. By Gilbert Thomas Morgan and Frances Mary Gore Mickiethwait	51	614
38. A simple manometer for vacuum distillation. By Norman Leslie Gebhard	51	—
39. Researches on the anthraquinones. By William Henry Bentley and Charles Weizmann	52	435
40. The formation of 4-pyrone compounds from acetylenic acids. Part I. By Siegfried Ruhemann	52	431
41. The action of mustard oils on the ethyl esters of malonic and cyanoacetic acids. By Siegfried Ruhemann	53	621
42. The triazo-group. Part II. Azoimides of propionic ester and of methyl ethyl ketone. By Martin Onslow Forster and Hans Eduard Fierz	54	669
43. Brazilin and hæmatoxylin. Part VIII. Synthesis of brazilinic acid, the lactones of dihydrobrazilinic and dihydrohæmatoxylinic acids, anhydrobrazilic acid, &c. The constitution of brazilin, hæmatoxylin, and their derivatives. By William Henry Perkin, jun., and Robert Robinson	54	489
March 5th.		
44. The solubility of iodine in water. By Harold Hartley and Norman Phillips Campbell	58	741
45. Nitro-derivatives of *o*-xylene. (Preliminary note.) By Arthur William Crossley and Nora Renouf	58	—
46. Substituted dihydrobenzenes. Part II. 1 : 1-Dimethyl-$\Delta^{2:4}$-dihydrobenzene and 1 : 1-dimethyl-$\Delta^{2:5}$-dihydrobenzene. By Arthur William Crossley and Nora Renouf	59	629
47. The viscosity of aqueous pyridine solutions. By Albert Ernest Dunstan and Ferdinand Bernard Theodore Thole	59	561
48. The action of thionyl chloride on the methylene ethers of catechol derivatives. Part II. Piperonyloin, piperil, and hydropiperoin. By George Barger and Arthur James Ewins	60	735
49. Traces of a new tin-group element in thorianite. By Clare de Brereton Evans	61	667

	Page in Proceedings.	Page in Transactions.
50. The sulphination of phenolic ethers and the influence of substituents. By Samuel Smiles and Robert Le Rossignol	61	745
51. The relation between unsaturation and optical activity. Part II. Alkaloid salts of corresponding saturated or unsaturated acids. By Thomas Percy Hilditch	61	700
52. The wandering of bromine in the transformation of nitroaminobromobenzenes. By Kennedy Joseph Previté Orton and Constance Pearson	62	725
53. A new isomeride of vanillin occurring in the root of a species of Chlorocodon. (Preliminary note.) By Ernest Goulding and Russell George Pelly	62	—
54. The volatile oil of the leaves of Ocimum viride. (Preliminary note.) By Ernest Goulding and Russell George Pelly	63	—
55. Experiments on the synthesis of the terpenes. Part XII. Synthesis of terpins, terpineols, and terpenes derived from the methyl*iso*propyl*cyclo*pentanes, $Me{\cdot}C_5H_8{\cdot}CHMe_2$. By Walter Norman Haworth and William Henry Perkin, jun.	64	573
56. The initial change of the radium emanation. By Nevil Vincent Sidgwick and Henry Thomas Tizard	64	—
March 19th.		
57. A new form of pyknometer. By William Robert Bousfield	69	679
58. The action of heat on α-hydroxycarboxylic acids. Part IV. Racemic αα′-dihydroxyadipic acid and meso-αα′-dihydroxyadipic acid. By Henry Rondel Le Sueur	70	716
59. The spontaneous crystallisation of sodium sulphate solutions. By Harold Hartley, Bernard Mouat Jones, and George Adrian Hutchinson	70	825
60. Constitution of hydroxyazo-compounds. Action of diazomethane and of mercuric acetate. By Clarence Smith [and, in part, Alec Duncan Mitchell]	70	842
61. Orthobromophenols and some bromonitrophenols. By Philip Wilfred Robertson	73	788
62. The constitution of thiocyanates containing an electronegative group. By Augustus Edward Dixon and John Taylor	73	684
63. The quantitative conversion of aromatic hydrazines into diazonium salts. By Frederick Daniel Chattaway	74	852
64. Quantitative separation of thallium from silver. By James Frederick Spencer and Margaret Le Pla	75	858
65. Molecular volumes of the nitrites of silver, mercury, and the alkali metals. By Prafulla Chandra Rây	75	997
66. Lithium nitrite and its decomposition by heat. By Prafulla Chandra Rây	75	—
67. The existence in aqueous solutions of a univalent cadmium ion, a subvalent thallium ion, and a bivalent bismuth ion. By Henry George Denham	76	833

	Page in Proceedings.	Page in Transactions.
68. Note on the oxidation of phenylhydrazine by Caro's acid. By John Cannell Cain	76	—
69. Some reactions of keten. By Frances Chick and Norman Thomas Mortimer Wilsmore	77	—
70. Para- and meta-nitrosoacetanilide. By John Cannell Cain	78	681
71. Labile isomerism among acyl-salicylamides and acyl-hydroxyamines. By Arthur Walsh Titherley	78	—
April 2nd.		
72. Rate of hydrolysis of chloroacetates, bromoacetates, and α-chlorohydrin by water and by alkali, and the influence of neutral salts on the reaction velocities. (Preliminary note.) By George Senter	89	—
73. The constituents of Cyprus origanum oil. Isolation of a new terpene "origanene." By Samuel Shrowder Pickles	91	862
74. The displacement of halogen in *l*-phenylchloroacetic acid by hydroxy- and methoxy-groups. A contribution to the chemistry of the Walden inversion. By Alex. McKenzie and George William Clough	91	811
75. The condensation of epichlorohydrin with phenols. By David Runciman Boyd and Ernest Robert Marle.	92	838
76. A new general method of preparing diazonium bromides. By Frederick Daniel Chattaway	93	958
77. The absorption spectrum of triphenylmethane. By Alfred Godfrey Gordon Leonard	93	—
78. The nature of the impurity found in preparations of triphenylmethane. By Walter Noel Hartley	94	—
79. The constitution of co-ordinated compounds. By Samuel Henry Clifford Briggs	95	1564
80. A combined stopcock and capillary connecting tube for gas burettes. By Arthur Edwin Hill	95	—
81. The hydrolysis of amygdalin by emulsin. Part I. By Samuel James Manson Auld	97	1251
82. Complex nitrites containing potassium and lead. (Preliminary note.) By Andrew Norman Meldrum.	97	—
83. The composition and formula of Wells' potassium lead periodide. By Andrew Norman Meldrum	97	—
84. The molecular complexity of amides in various solvents. By Andrew Norman Meldrum and William Ernest Stephen Turner	98	876
85. The optical activity of compounds having simple molecular structure. By William Jackson Pope and John Read	99	794
86. Acetylketen: a polymeride of keten. By Frances Chick and Norman Thomas Mortimer Wilsmore	100	946
87. Saponification of ethyl formate by water in presence of acids as catalytic agents. By Arthur Lapworth	100	—

	Page in Proceedings.	Page in Transactions.
88. The triazo-group. Part III. Bistriazo-derivatives of ethane and of acetic ester. By Martin Onslow Forster, Hans Eduard Fierz, and Walter Phillip Joshua	102	1070
May 7th.		
89. The refraction and dispersion of triazo-compounds. By James Charles Philip.....	114	918
90. The dissociation constants of triazoacetic and α-triazopropionic acids. By James Charles Philip	114	925
91. The fermentation of mannose and lævulose by yeast-juice. (Preliminary note.) By Arthur Harden and William John Young.....	115	—
92. The constituents of olive leaves. By Frederick Belding Power and Frank Tutin.....	117	891
93. The constituents of olive bark. By Frederick Belding Power and Frank Tutin.....	117	904
94. The reaction of diazonium salts with mono- and dihydric phenols and with naphthols. By Kennedy Joseph Previté Orton and Reginald William Everatt.....	118	1010
95. The condensation of benzoin with methyl alcohol. By James Colquhoun Irvine and David McNicoll	119	950
96. The mutual solubility of 2-methylpiperidine and water. By Otto Flaschner and Basil MacEwen.	119	1000
97. The melting points of the anilides, *p*-toluidides, and α-naphthalides of the normal fatty acids. By Philip Wilfred Robertson.....	120	1033
98. The absorption spectrum of camphor. By Walter Noel Hartley	120	961
99. The viscosity of solutions. By Charles Edward Fawsitt	121	1004
100. The action of fused potassium hydroxide and of hydrogen peroxide on cholesterol. (Preliminary note.) By Robert Howson Pickard and Joseph Yates	121	—
101. The volumetric estimation of silver. By William Robert Lang and J. C. Woodhouse.....	122	1037
102. A criticism of Werner's theory, and the constitution of complex salts. By John Albert Newton Friend.....	122	1006
103. The action between potassium sulphite and potassium pentathionate. By Edward Divers.....	122	—
104. Note on phenolic thetines and their action with benzoyl chloride. By Edward de Barry Barnett and Samuel Smiles.....	123	—
105. The relation between dielectric constant and chemical constitution. Part I. Stereoisomeric compounds. By Alfred Walter Stewart.....	124	1059
106. An apparatus for determining the specific inductive capacity of organic liquids. By Alfred Walter Stewart.....	124	1062

	Page in Proceedings.	Page in Transactions.
107. The influence of solvents on the rotation of optically active compounds. Part XII. Ethyl tartrate in aromatic halogen derivatives. By Thomas Stewart Patterson and David Paterson McDonald	125	936
108. A new test for silver. By Arnold William Gregory	125	—
109. The spontaneous crystallisation of substances which form a continuous series of mixed crystals: mixtures of naphthalene and β-naphthol. By Henry Alexander Miers and Florence Isaac	125	927
May 21st.		
110. Hydroaromatic ketones. (Preliminary note.) By Arthur William Crossley and Charles Gilling	130	—
111. The sulphides and oxysulphides of silicon. By Irvine Giles Rankin and Sidney Montagu Revington	131	—
112. Apparatus for experiments at high temperatures and pressures and its application to the study of carbon. By Richard Threlfall	131	1333
113. Acids as accelerators in the acetylation of amino-groups. By Alice Emily Smith and Kennedy Joseph Previté Orton	132	1242
114. The chemical action of radium emanation. Part III. On water and certain gases. By Alexander Thomas Cameron and Sir William Ramsay, K.C.B.	132	966
115. The chemical action of radium emanation. Part IV. On water. By Alexander Thomas Cameron and Sir William Ramsay, K.C.B.	133	992
116. Titani-dihydroxymaleic acid and the detection of titanium By Henry John Horstman Fenton	133	1064
117. The preparation of diselenides. Dibenzyl diselenide. (Preliminary note.) By Thomas Slater Price and Lionel Manfred Jones	134	—
118. The optical and sensitising properties of the *iso*cyanine dyes. By Samuel Edward Sheppard	134	15*
119. The polarimetric study of intramolecular rearrangement in inactive substances. By Thomas Stewart Patterson and Andrew McMillan	135	1041
120. Mercuric zinc cyanide. A correction. By Wyndham Rowland Dunstan	135	—
121. Ethyl 6-methyl-2-pyrone-3 : 5-dicarboxylate and its derivatives. By John Lionel Simonsen	136	1022
122. Contributions to the chemistry of the amidines. Part II. 2-Anilinobenzoxazole and the supposed anilodihydrobenzoxazole. By George Young and Albert Ernest Dunstan	136	1052
123. The slow decomposition of ammonium chromate, dichromate, and trichromate by heat. By Walter Craven Ball	136	—

	Page in Proceedings.	Page in Transactions.
June 4th.		
124. The interaction of copper and nitric acid in presence of metallic nitrates considered with reference to the existence of hydrates in solution. By Edward Henry Rennie, Alfred James Higgin, and William Ternent Cooke	141	1162
125. The triazo-group. Part IV. Allylazoimide. By Martin Onslow Forster and Hans Eduard Fierz	143	1174
126. Aromatic arsonic and arsinic acids. By Frank Lee Pyman and William Colebrook Reynolds	143	1180
127. Condensation products from aminopinenedicarboxylic acid. By William Godden	144	1171
128. A delicate test for bromides alone or in solution with chlorides. By James Sprunt Jamieson	144	—
129. Experiments on the synthesis of 1-methyl*cyclo*hexylidene-4-acetic acid, $CHMe<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C{:}CH\cdot CO_2H$. Part I. By William Henry Perkin, jun., and William Jackson Pope	145	1075
130. A method for the measurement of rate of change in solid alloys. (Preliminary note.) By Guy Dunstan Bengough	145	—
131. Viscosity determinations at high temperatures. By Charles Edward Fawsitt	146	1299
132. Dinitrodiphenylamine-*o*-sulphonic acids. (Preliminary note.) By Samuel Smiles	147	—
133. The study of the absorption spectra of the hydrocarbons isolated from the products of the action of aluminium chloride on naphthalene. By Annie Homer and John Edward Purvis	147	1319
134. The synthesis and constitution of certain pyranol salts related to brazilein and hæmatein. By William Henry Perkin, jun., Robert Robinson, and [in part] Maurice Russell Turner	148	1085
135. Brazilin, hæmatoxylin, and their derivatives. Part IX. On brazilein, hæmatein, and their derivatives. By Paul Engels, William Henry Perkin, jun., and Robert Robinson	148	1115
136. The effect of constitution on the optical activity of nitrogen compounds. By Reginald W. Everatt	148	1225
137. The electrolytic oxidation of some hydroxybenzoic acids. By Arthur George Perkin and Frederick Mollwo Perkin	149	1186
138. Note on morindin. By Arthur George Perkin	149	—
139. Some esters of arsenious acid. By William Robert Lang, John Francis Mackey, and Ross Aitken Gortner	150	1364
140. α-Methylcamphor and fenchone. By Walter Hamis Glover	151	1285
141. Ester hydrolysis and theories of esterification. By Arthur Lapworth	152	—

	Page in Proceedings.	Page in Transactions.
142. Experiments on the formation and hydrolysis of esters, acetals, and allied compounds. (Preliminary note.) By Edward Fitzgerald and Arthur Lapworth	153	—
June 18th.		
143. The thermal decomposition of hydrocarbons. Part I. [Methane, ethane, ethylene, and acetylene.] By William Arthur Bone and Hubert Frank Coward ...	167	1197
144. The rusting of iron. By William Augustus Tilden ...	169	1356
145. Studies on zirconium. By Edgar Wedekind and Samuel Judd Lewis	170	—
146. The constituents of Canadian hemp. Part I. Apocynin. By Horace Finnemore.....	171	1513
147. A new synthesis of apocynin. By Horace Finnemore.	171	1520
148. The constitution of the diazonium perbromides. By Frederick Daniel Chattaway	172	—
149. Cholestenone. By Charles Dorée and John Addyman Gardner	173	1328
150. Solubility of silver chloride in mercuric nitrate solution. By Bertram Hayward Buttle and John Theodore Hewitt	173	1405
151. The relation between absorption spectra and chemical constitution. Part IX. The nitroso- and nitro-groups. By Edward Charles Cyril Baly and Cecil Henry Desch	173	1747
152. Benzeneazo-2-pyridone. By William Hobson Mills and Sibyl T. Widdows	174	1372
153. The electrolytic chlorination of the salts of some organic acids. By John Kenneth Harold Inglis and Fred Wootton.....	174	1592
154. The action of nitrous gases on di*cyclo*pentadiene. By Alexander Rule	175	1560
155. An alternative structure for the supposed stereo-isomeric α-osazones. By Frederick Daniel Chattaway	175	—
156. The formation of 4-pyrone compounds from acetylenic acids. Part II. By Siegfried Ruhemann	177	1281
157. The fluorescence of platinocyanides. By Leonard Angelo Levy	178	1446
158. The preparation of disulphides. Part II. The action of alkalis on sodium alkyl thiosulphates. By Thomas Slater Price and Douglas Frank Twiss	179	1395
159. Note on the formation of lead ethoxide. By Frederick Mollwo Perkin	179	—
160. Some reactions of phenylhydrazine with metallic cyanides and other salts. By Robert de Jersey Fleming Struthers.....	179	—
161. The formation of polyiodides in nitrobenzene solution. Part III. The chemical dissociation of the polyiodides of the alkali metals and ammonium radicles. By Harry Medforth Dawson.....	181	1308

	Page in Proceedings.	Page in Transactions.
162. The hydrolysis of amygdalin by emulsin. Part II. By Samuel James Manson Auld	181	1276
163. A new form of potash bulb. By Arthur Edwin Hill.	182	—
Papers received during the vacation and published, or passed for publication, in the Transactions:		
164. The use of the micro-balance for the determination of electrochemical equivalents and for the measurement of densities of solids.* By Otto Brill and Clare de Brereton Evans	185	1442
165. The preparation of disulphides. Part III. The nitrobenzyl disulphides. By Thomas Slater Price and Douglas Frank Twiss	185	1401
166. The relation between unsaturation and optical activity. Part III. Optically active salts of acids containing adjacent unsaturated groups. By Thomas Percy Hilditch	186	1388
167. The constitution of glucose derivatives. Part I. Glucose-anilide, -oxime, and -hydrazone. By James Colquhoun Irvine and Robert Gilmour	186	1429
168. The *cis*- and *trans*-modifications of 1-methyl*cyclo*hexan-2-ol-4-carboxylic acid, and their conversion into 1-methyl-Δ^1-*cyclo*hexene-4-carboxylic acid. By Andrew Norman Meldrum and William Henry Perkin, jun	187	1416
169. Studies on the viscosity and conductivity of some aqueous solutions. Part I. Solutions of sucrose, hydrogen chloride, and lithium chloride. By W. Heber Green	187	2023
170. Studies on the viscosity and conductivity of some aqueous solutions. Part II. Mixtures of solutions of sucrose and lithium chloride; a contribution towards the elucidation of the connexion between ionic mobility and the fluidity of the solution. By W. Heber Green	187	2049
171. The reduction of refractory oxides by carbon. By Harold Cecil Greenwood	188	1483
172. The production of ferro-alloys. By Harold Cecil Greenwood	189	1496
173. The rapid electroanalytical deposition and separation of metals. Part II. Antimony and tin. The employment of a diaphragm. By Henry Julius Salomon Sand	189	1572
174. The measurement of a homogeneous chemical change in a gas. (The thermal decomposition of ozone.) By Herbert Edmund Clarke and David Leonard Chapman	190	1638
175. The proteins of egg-yolk. By Robert Henry Aders Plimmer	190	1500

* This paper was taken as read at the meeting of May 21st, 1908.

	Page in Proceedings.	Page in Transactions.
176. The conductivities of the α-oximino-fatty acids. By John Kenneth Harold Inglis and Lottie Emily Knight	191	1595
177. Studies of the perhalogen salts. Part II. By Charles Kenneth Tinkler	191	1611
178. The formation of ethers from compounds of the benzoin type. By James Colquhoun Irvine and David McNicoll	191	1601
179. Aromatic α-disulphones. By Thomas Percy Hilditch.	192	1520
180. The action of bromine on β-hydrindone. By Norman Allen Creeth and Jocelyn Field Thorpe	192	1507
181. On polymorphism, with especial reference to sodium nitrate and calcium carbonate. By William Barlow and William Jackson Pope	193	1528
182. The oxidation of phosphorous acid by iodine. By Bertram Dillon Steele	193	2203
183. The direct interaction of magnesium and alkyl halides. By James Frederick Spencer and Mary S. Crewdson	194	1821
184. The interaction of the metals of the aluminium group and organic halogen derivatives. By James Frederick Spencer and Marion L. Wallace	194	1827
185. The relation between unsaturation and optical activity. Part IV. The relative influence of bi-, quadri-, and sexa-valent sulphur on rotatory power. By Thomas Percy Hilditch	195	1618
186. Oxidations of hydrocarbons of the benzene series. Part II. Substances containing a negative radicle. By Herbert Drake Law and Frederick Mollwo Perkin	195	1633
187. Coprosterol. Part I. By Charles Dorée and John Addyman Gardner	195	1625
188. The spontaneous crystallisation of solutions of some alkali nitrates. By Bernard Mouat Jones	195	1739
189. Syntheses with phenol derivatives containing a mobile nitro-group. Part I. The interaction of 2 : 3 : 5-trinitro-4-acetylaminophenol and amines. By Raphael Meldola and James Gordon Hay	197	1659
190. The constituents of the expressed oil of nutmeg. By Frederick Belding Power and Arthur Henry Salway	197	1653
191. The preparation of disulphides. Part IV. Esters of dithiodiglycollic and dithiodilactylic acids. By Thomas Slater Price and Douglas Frank Twiss	198	1645
192. Contributions to the chemistry of the cholesterol group. Part I. The action of hydrogen peroxide and of fused potassium hydroxide on cholesterol. By Robert Howson Pickard and Joseph Yates	199	1678
193. Derivatives of *S*-phenylphenazothionium. Part II. By Samuel Smiles and Thomas Percy Hilditch	199	1687
194. The trithionates and tetrathionates of the alkali metals. Part I. By John Edwin Mackenzie and Hugh Marshall	199	1726

	Page in Proceedings.	Page in Transactions.
195. The synthesis of complex acridines. By Percy Corlett Austin	200	1760
196. A reaction distinguishing phosphoprotein from nucleoprotein, and the distribution of phosphoproteins in tissues. By Robert Henry Aders Plimmer and Frederick Hughes Scott	200	1699
197. The colouring matters of the stilbene group. Part V. The action of caustic alkalis on derivatives of para-nitrotoluene. By Arthur George Green and James Baddiley	201	1721
198. The solubility of lime in water. By Gerald Tattersall Moody and Lewis Thomas Leyson	202	1767
October 22nd.		
199. The relationship of colour and fluorescence to constitution. Part II. Rhodamines of mellitic acid. By Oswald Silberrad and Charles Smart Roy	204	—
200. Constitution of the salts of the phthaleins and the cause of colour in the triphenylmethane series. By Arthur George Green	206	—
201. The relation between absorption spectra and chemical constitution. Part X. Unsaturated acids of the benzene series. By Edward Charles Cyril Baly and Konrad Schaefer	207	1808
202. Relation between chemical constitution and physiological action in certain substituted aminoalkyl esters. By Frank Lee Pyman	208	1793
203. The passage of hydrogen through a palladium septum, and the pressure which it produces. By Demetrius Tsakalotos	208	—
204. Constitution of the phthaleins of mellitic and pyromellitic acids. By Oswald Silberrad	209	—
205. A new form of gas burette. By Arthur Edwin Hill	210	1857
206. A molecular compound of trinitroacetylaminophenol and β-naphthol. By Raphael Meldola and James Gordon Hay	210	—
207. The products of reduction of azoxybenzene. (Preliminary note.) By Leslie Hamilton Berry	211	—
208. The chlorination of para-nitroaniline. By Bernhard Flürscheim	211	1772
209. Syntheses with the aid of monochloromethyl ether. Part I. The action of monochloromethyl ether on the sodium derivatives of ethyl malonate and ethyl *iso*propylmalonate. By John Lionel Simonsen	212	1777
210. The effect of constitution on the rotatory power of optically active nitrogen compounds. Part III. By Reginald William Everatt and Humphrey Owen Jones	212	1789
211. Studies on the cobaltinitrites. By Mary Cunningham and Frederick Mollwo Perkin	212	

	Page in Proceedings.	Page in Transactions.
212. The relation between viscosity and chemical constitution. Part II. The existence of racemic compounds in the liquid state. By Albert Ernest Dunstan and Ferdinand Bernard Thole	213	1815
213. The formation of polyiodides in nitrobenzene solution. Part IV. The electrolytic dissociation of the polyiodides of the alkali metals and ammonium radicles. By Harry Medforth Dawson and Colin Gyrth Jackson	213	2063
214. The direct action of radium on copper and gold. By Edgar Philip Perman	214	1775
215. The atomic volumes of phosphorus. Part II. Phosphorus and bromine. By Edmund Brydges Rudhall Prideaux	214	—
216. Isomeric chromous chlorides. By Elizabeth Mary Rich	215	—
217. The relative atomic weights of hydrogen and chlorine. By Robert Whytlaw Gray and Frank Playfair Burt	215	—
218. The interaction of hydrogen dioxide and sulphides By Maud Gazdar and Samuel Smiles	216	1833
219. The influence of solvents on the rotation of optically active compounds. Part XIII. Ethyl tartrate in aromatic nitro-derivatives. Influence of temperature change on rotation in solution. By Thomas Stewart Patterson	216	1836
220. The isomeric menthols. (Preliminary note.) By Robert Howson Pickard and William Oswald Littlebury ...	217	—
November 5th.		
221. The direct union of carbon and hydrogen. Synthesis of methane. By William Arthur Bone and Hubert Frank Coward	222	1975
222. The relation between absorption spectra and chemical constitution. Part XI. Some aromatic hydrocarbons. By Edward Charles Cyril Baly and William Bradshaw Tuck	223	1902
223. Organic derivatives of silicon. Part VII. The synthesis of *dl*-sulphobenzylethyl*iso*butylsilicyl oxide. By Bernard Dunstan Wilkinson Luff and Frederic Stanley Kipping	224	2004
224. The relation between viscosity and chemical constitution. Part III. The enol-ketonic tautomerism. By Albert Ernest Dunstan and James Arthur Stubbs	224	1919
225. The chlorination of methyl derivatives of pyridine. Part II. 2-Methylpyridine. By William James Sell	225	1993
226. The chlorine derivatives of pyridine. Part IX. Preparation and orientation of 3 : 5-dichloropyridine. By William James Sell	225	1997

	Page in Proceedings.	Page in Transactions.
227. The chlorine derivatives of pyridine. Part X. Orientation of 2 : 3 : 5-trichloropyridine. By William James Sell	225	2001
228. The triazo-group. Part V. Resolution of α-triazopropionic acid. By Martin Onslow Forster and Hans Eduard Fierz	226	1859
229. The triazo-group. Part VI. Triazoethyl alcohol and triazoacetaldehyde. By Martin Onslow Forster and Hans Eduard Fierz	227	1865
230. Contribution to the chemistry of the cholesterol group. Part II. Some oxidation products of sitosterol. By Robert Howson Pickard and Joseph Yates	227	1928
231. Experiments on the synthesis of the terpenes. Part I (cont.). Resolution of *dl*-1-methyl-Δ^1-*cyclo*hexene-4-carboxylic acid and synthesis of the optically active modifications of terpineol. By Kenneth Fisher and William Henry Perkin, jun.	228	1871
232. Experiments on the synthesis of the terpenes. Part XIII. Synthesis of *iso*carvestrene ($\Delta^{6:8(9)}$-*m*-menthadiene) and its derivatives. By Kenneth Fisher and William Henry Perkin, jun.	228	1878
233. Colour and constitution of azomethine compounds. Part II. By Frank George Pope and Robert Fleming.	228	1914
234. Aromatic arsonic acids. By Marmaduke Barrowcliff, Frank Lee Pyman, and Frederic George Percy Remfry	229	1893
235. The condensation of salicylaldehyde and benzamide. By Arthur Walsh Titherley and Morris Edgar Marples	229	1933
236. The coumarin condensation. By Arthur Clayton	229	2016
237. Experiments on the synthesis of 1-methyl*cyclo*hexylidene-4-acetic acid. Part II. By Victor John Harding, Walter Norman Haworth, and William Henry Perkin, jun.	230	1943
November 19th.		
238. Meteloidine : a new solanaceous alkaloid. By Frank Lee Pyman and William Colebrook Reynolds	234	2077
239. The affinity of certain alkaloids for hydrochloric acid. By Victor Herbert Veley	234	2114
240. The relation between absorption spectra and chemical constitution. Part XII. Some amino-aldehydes and -ketones of the aromatic series. By Edward Charles Cyril Baly and Effie Gwendoline Marsden	235	2108
241. Organic derivatives of silicon. Part VIII. The resolution of *dl*-sulphobenzylethyl*iso*butylsilicyl oxide and the properties of the optically active acids. By Bernard Dunstan Wilkinson Luff and Frederic Stanley Kipping	236	2099

	Page in Proceedings.	Page in Transactions.
242. The action of phosphorus pentachloride on the methylene ethers of catechol derivatives. Part III. The cyclic carbonates of dichloro-ethyl- and -propyl-catechol. By George Barger	237	2081
243. The synthesis of thionaphthen derivatives from styrenes and thionyl chloride. By George Barger and Arthur James Ewins	237	2086
244. The affinity constants of bases as determined by the aid of methyl-orange. By Victor Herbert Veley	238	2122
245. Study of the constitution and properties of the rhodanides of inorganic radicles. By Augustus Edward Dixon and John Taylor	238	2148
246. The electrical conductivity of phosphoric acid. By Harry Edward William Phillips	239	59*
247. The molecular volumes of the nitrites of barium, strontium, and calcium. By Prafulla Chandra Rây	240	—
248. The formation of some carbides. By John Norman Pring	240	2101
249. 4-Chloroacenaphthene. By Holland Crompton and Eva Richardis Cyriax	241	—
250. Some molecular compounds of styphnic and picric acids. By Charles Stanley Gibson	241	2098
December 3rd.		
251. Double salts of potassium iodide with mercuric iodide and dimercuriodocamphor in organic solvents. By James Ernest Marsh and Robert de Jersey Fleming Struthers	266	—
252. The action of mercuric iodide on ketones in alkaline solution. By James Ernest Marsh and Robert de Jersey Fleming Struthers	266	—
253. The condensation of camphor with mercuric iodide. By James Ernest Marsh and Robert de Jersey Fleming Struthers	267	—
254. The relation between absorption spectra and chemical constitution. Part XIII. Some pyrones and allied compounds. By Edward Charles Cyril Baly, John Norman Collie, and Herbert Edmeston Watson	268	—
255. Organic derivatives of arsenic. Part I. Dicamphoryl-arsinic acid. By Gilbert T. Morgan and Frances M. G. Micklethwait	268	2144
256. Tellurium dicyanide. By Herbert Edwin Cocksedge.	269	2175
257. Boron thiocyanate. By Herbert Edwin Cocksedge	270	2177
258. The viscosity of fuming sulphuric acid. By Albert Ernest Dunstan and Robert William Wilson	270	2179
259. The decomposition of carbon dioxide by the silent electric discharge. By Alfred Holt, jun.	271	30*
260. Note on oxalyl chloride. By Humphrey Owen Jones and Hubert Sanderson Tasker	271	—

	Page in Proceedings.	Page in Transactions.
261. The densities of krypton and xenon. By Richard B. Moore	272	2181
262. The action of reducing agents on tannic and gallic acids. By Walter Myers Gardner and Herbert Henry Hodgson	272	—
263. The action of iodine on phenols and a modified process for the estimation of tannic acid. By Walter Myers Gardner and Herbert Henry Hodgson	273	—
264. Ester catalysis and a modification of the theory of acids. By Edward Fitzgerald and Arthur Lapworth	274	2163
265. An examination of the conception of hydrogen ions in catalysis, salt formation, and electrolytic conduction. By Arthur Lapworth	275	2187
December 17th.		
266. Silicon researches. Part XI. Silicotetrapyrrole. By James Emerson Reynolds	279	—
267. Silicon researches. Part XII. The action of silicochloroform on potassium pyrrole. By James Emerson Reynolds	279	—
268. Silicon researches. Part XIII. Silicon halides and pyridine, acetonitrile, etc. By James Emerson Reynolds	280	—
269. The affinity values of tropine and its derivatives. By Victor Herbert Veley	280	1*
270. Hydroaromatic ketones. Part I. Synthesis of trimethyl*cyclo*hexenone (*iso*phorone) and some homologues. By Arthur William Crossley and Charles Gilling	281	19*
271. Note on the determination of the rate of chemical change by measurement of the gases evolved. By John Cannel Cain and Frank Nicoll	282	—
272. The formation and reactions of imino-compounds. Part VII. The formation of 1 : 3-naphthylenediamine from β-imino-α-cyano-γ-phenylpropane. By Stanley Robert Best and Jocelyn Field Thorpe	283	8*
273. The absorption spectra of para-benzoquinone, quinol, and quinhydrone in the state of vapour and in solution. By Walter Noel Hartley and Alfred Godfrey Gordon Leonard	284	34*
274. The constitution of para-benzoquinone. By Walter Noel Hartley	285	52*
275. Benzyl sulphoxide: a possible example of dynamic isomerism. By John Armstrong Smythe	285	—
276. The chemical dynamics of the reactions between sodium thiosulphate and organic halogen compounds. Part III. By Arthur Slator and Douglas Frank Twiss	286	—

	Page in Proceedings.	Page in Transactions.
277. Note on the optical rotatory power of menthyl cinnamate. By Thomas Percy Hilditch	286	—
278. Liberation of iodine from hydriodic acid by certain halogenated malonyl derivatives. By Martha Annie Whiteley	288	—
EXTRA MEETING.		
March 26th.—Annual General Meeting	81	763

* Papers printed in the Transactions for 1909 are distinguished by an asterisk after the Page number. Where no reference is given to the Transactions, the paper has so far appeared only in the Proceedings.

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ADDITIONS TO THE LIBRARY DURING THE YEAR 1908.

Abegg, *R.* See **Handbuch der anorganischen Chemie.**

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Applebey, M. P., 22.
Auld, S. J. M., 97, 181.
Austin, P. C., 200.

Baddiley, J., 201.
Ball, W. C., 136.
Baly, E. C. C., 173, 207, 223, 235, 268.
Barger, G., 50, 60, 237.
Barlow, W., 193.
Barnett, E. de B., 123.
Barrowcliff, M., 229.
Bengough, G. D., 145.
Bentley, W. H., 52.
Berry, L. H., 211.
Best, S. R., 283.
Blackman, P., 8.
Bone, W. A., 167, 222.
Bousfield, W. R., 69.
Boyd, D. R., 92.
Briggs, S. H. C., 94.
Brill, O., 185.
Burt, F. P., 215.
Buttle, B. H., 173.

Cain, J. C., 76, 78, 282.
Cameron, A. T., 132, 133.
Campbell, N. P., 47, 58.
Chapman, D. L., 190.
Chattaway, F. D., 10, 74, 93, 172, 175.
Chick, F. (Miss), 77, 100.
Clarke, H. E., 190.
Clayton, A., 26, 229.
Clough, G. W., 91.
Cocksedge, H. E., 269, 270.
Cohen, J. B., 15.
Collie, J. N., 268.
Cooke, W. T., 141.
Coward, H. F., 167, 222.
Creeth, N. A., 192.
Crewdson, M. S. (Miss), 194.
Crompton, H., 241.
Cross, W. E., 15.
Crossley, A. W., 58, 59, 130, 281.
Cumming, A. C., 28.
Cunningham, M. (Miss), 212.
Cyriax, E. R. (Mrs.), 241.

Dawson, H. M., 26, 181, 213.
Denham, H. G., 14, 76.
Desch, C. H., 173.
Divers, E., 16, 122.
Dixon, A. E., 73, 238.
Dorée, C., 173, 196.
Dunstan, A. E., 59, 136, 213, 224, 270.
Dunstan, W. R., 135.

Engels, P., 148.
Evans, C. de B. (Miss), 60, 185.
Everatt, R. W., 118, 148, 212.
Ewins, A. J., 60, 237.

Fawsitt, C. E., 121, 146.
Fenton, H. J. H., 133.
Fierz, H. E., 54, 102, 143, 226, 227.
Finnemore, H., 171.
Fisher, K., 228.
Fitzgerald, E., 153, 274.
Flaschner, O., 119.
Fleming, R., 228.
Flürscheim, B., 211.
Forster, M. O., 8, 54, 102, 143, 226, 227.
Fox, J. J., 6.
Friend, J. A. N., 14, 122.

Gardner, J. A., 173, 196.
Gardner, W. M., 272, 273.
Gazdar, M. (Miss), 216.
Gebhard, N. L., 51.
Gibson, C. S., 241.
Gilling, C., 130, 281.
Gilmour, R., 186.
Gittins, J. M., 14.

Glover, W. H., 151.
Godden, W., 144.
Gortner, R. A., 150.
Goulding, E., 62, 63.
Gray, R. W., 215.
Green, A. G., 201, 206.
Green, W. H., 187.
Greenwood, H. C., 188, 189.
Gregory, A. W., 125.

Harden, A., 115.
Harding, V. J., 230.
Hartley, H., 22, 47, 58, 70.
Hartley, W. N., 94, 120, 284, 285.
Haworth, W. N., 64, 230.
Hay, J. G., 197, 210.
Henderson, G. G., 31.
Heilbron, I. M., 31.
Hewitt, J. T., 6, 173.
Higgin, A. J., 141.
Hilditch, T. P., 61, 186, 192, 195, 199, 286.
Hill, A. E., 95, 182, 210.
Hill, J. R., 28.
Hodgson, H. H., 272, 273.
Holmes, H., 8.
Holt, A., jun., 271.
Homer, A. (Miss), 147.
Hooton, W. M., 27.
Hutchinson, G. A., 70.

Inglis, J. K. H., 174, 191.
Irvine, J. C., 119, 186, 191.
Isaac, F. (Miss), 30, 125.

Jackson, C. G., 26, 213.
Jaeger, F. M., 29.
Jamieson, J. S., 144.
Jones, B. M., 70, 196.
Jones, H. O., 28, 212, 271.
Jones, L. M., 134.
Joshua, W. P., 102.

Kipping, F. S., 12, 25, 47, 224, 236.
Knight, L. E. (Miss), 191.

Lamplough, F. E. F., 29.
Lang, W. R., 122, 150.
Lapworth, A., 100, 152, 153, 274, 275.
Law, H. D., 195.
Leonard, A. G. G., 93, 284.
Le Pla, M. (Miss), 75.
Le Rossignol, R., 61.
Le Sueur, H. R., 70.
Levy, L. A., 178.
Lewis, S. J., 170.
Leyson, L. T., 202.
Littlebury, W. O., 217.
Luff, B. D. W., 224, 236.

McDonald, D. P., 125.
MacEwen, B., 119.
McKenzie, A., 25, 91.
Mackenzie, J. E., 199.
Mackey, J. F., 150.
McMillan, A., 135.
McNicoll, D., 119, 191.
Marle, E. R., 92.
Marples, M. E., 229.
Marsden, E. G. (Miss), 235.
Marsden, H., 12.
Marsh, J. E., 266, 267.
Marshall, H., 199.
Meldola, R., 197, 210.
Meldrum, A. N., 31, 97, 98, 187.
Micklethwait, F. M. G. (Miss), 48, 51, 268.
Miers, H. A., 125.
Mills, W. H., 174.
Mitchell, A. D., 70.
Moody, G. T., 202.
Moore, C. W., 12.
Moore, R. B., 272.
Morgan, G. T., 48, 51, 268.

Nicoll, F., 282.

Orton, K. J. P., 27, 62, 118, 132.

Patterson, T. S., 125, 135, 216.
Pearson, C. (Miss), 62.
Pelly, R. G., 62, 63.
Perkin, A. G., 149.
Perkin, F. M., 149, 179, 195, 212.
Perkin, W. H., jun., 54, 64, 145, 148, 187, 228, 230.
Perman, E. P., 214.
Philip, J. C., 114.
Phillips, H. A., 22.
Phillips, H. E. W., 239.
Pickard, R. H., 121, 199, 217, 227.
Pickles, S. S., 91.
Plimmer, R. H. A., 190, 200.
Poole, R. H., 47.
Pope, F. G., 24, 228.
Pope, W. J., 99, 145, 193.
Power, F. B., 117, 197.
Price, T. S., 134, 179, 185, 198.
Prideaux, E. B. R., 214.
Pring, J. N., 240.
Purvis, J. E., 147.
Pyman, F. L., 143, 208, 229, 234.

Ramsay, Sir W., K.C.B., 132, 133.
Rankin, I. G., 131.
Ray, P. C., 75, 240.
Read, J., 99.
Remfry, F. G. P., 229.
Rennie, E. H., 141.
Renouf, N. (Miss), 58, 59.
Revington, S. M., 131.

Reynolds, J. E., 279, 280.
Reynolds, W. C., 143, 234.
Rich, E. M. (Miss), 215.
Robertson, P. W., 73, 120.
Robinson, R., 54, 148.
Robison, R., 25.
Roy, C. S., 204.
Ruhemann, S., 52, 53, 177.
Rule, A., 175.

Salway, A. H., 197.
Sand H. J. S., 189.
Schaefer, K., 207.
Scott, F. H., 200.
Sell, W. J., 225.
Senter, G., 89.
Sheppard, S. E., 134.
Sidgwick, N. V., 64.
Silberrad, O., 22, 204, 209.
Simonsen, J. L., 136, 212.
Slade, R. E., 29.
Slator, A., 11, 286.
Smiles, S., 61, 123, 147, 199, 216.
Smith, A. E. (Miss), 27, 132.
Smith, C., 70.
Smythe, J. A., 285.
Spencer, J. F., 75, 194.
Steele, B. D., 193.
Stewart, A. W., 124.
Struthers, R. de J. F., 179, 266, 267.
Stubbs, J. A., 224.
Sudborough, J. J., 14.

Tasker, H. S., 271.
Taylor, J., 73, 238.
Thole, F. B. T., 59, 213.
Thomas, N. G., 22.
Thorpe, J. F., 12, 192, 283.
Threlfall, R., 131.
Tilden, W. A., 169.
Tinkler, C. K., 191.
Titherley, A. W., 78, 229.
Tizard, H. T., 64.
Tsakalotos, D., 208.
Tuck, W. B., 223.
Turner, M. R., 148.
Turner, W. E. S., 98.
Tutin, F., 23, 117.
Twiss, D. F., 179, 185, 198, 286.

Veley, V. H., 50, 234, 238, 280.

Wallace, M. L. (Miss), 194.
Watson, H. E., 268.
Wedekind, E., 170.
Weizmann, C., 52.
Whiteley, M. A. (Miss), 288.
Widdows, S. T. (Miss), 174.
Wilsmore, N. T. M., 77, 100.
Wilson, R. W., 270.
Wood, J. K., 15.
Woodhouse, J. C., 122.
Wootton, F., 174.
Wren, H., 25.

Yates, J., 121, 199, 227.
Young, G., 136.
Young, W. J., 115.

INDEX TO DISCUSSIONS.

Armstrong, H. E., 142, 168, 169.

Baly, E. C. C., 7, 9, 71, 236.
Bone, W. A., 168, 223.

Caldwell, R. J., 23.

Divers, E., 168.
Dunstan, A. E., 22, 60, 270.

Feilmann, M. E., 222.
Forster, M. O., 268, 269.

Green, A. G., 205.

Harden, A., 117.
Hartley, H., 23, 48, 59.
Hewitt, J. T., 8, 10, 24, 72, 236.
Hooper, G., 116.

Jeffers, E. H., 90.
Jowett, H. A. D., 169.

Lowry, T. M., 48, 222, 269.

McKenzie, A., 25, 92.
Marsh, J. E., 268.
Mills, E. J., 168.
Mitchell, H. V., 7.
Morgan, G. T., 49, 72, 207, 269.

Philip, J. C., 48.
Pyman, F. L., 144.

Ramsay, Sir W., 131, 144, 283.
Redgrove, H. S., 115.
Reynolds, W. C., 142.

Senter, G., 91, 270, 282.
Silberrad, O., 205, 206.
Smith, C., 72, 92.

Tilden, W. A., 170.
Tuck, W. B., 7.

Veley, V. H., 142, 235.

Young, G., 49.

INDEX OF SUBJECTS.

Absorption spectra. See under Photochemistry.

Acenaphthene styphnate, 241.

Acenaphthene, 4-chloro-, and its picrate, 241.

Acetals, formation and hydrolysis of, 153.

Acetanilide, *m*- and *p*-nitroso-, 78.

Acetic acid, mercuric salt, action of, on hydroxyazo-compounds, 70.

Acetic acid, ethyl ester, bistriazo-derivative of, 102.

Acetic acid, bromo- and chloro-, and their salts, rate of hydrolysis of, by water and by alkali, and the influence of neutral salts on the reaction velocities, 89.

cyano-, ethyl ester, action of phenylthiocarbimide on, 53.

Acetone, reaction of, with mercuric iodide in alkaline solution, 266.

Acetonitrile, additive compound of, with silicon tetrabromide, 280.

Acetophenone, reaction of, with mercuric iodide in alkaline solution, 267.

Acetovanillone. See Apocynin.

Acetylanhydropurpurogallonecarboxylic acid, 149.

1-Acetylanilinobenzoxazole, 136.

Acetylanthranilic acid, brucine and cinchonine salts, and their optical activity, 186

Acetylation of amino-groups, acids as accelerators in the, 132.

a-Acetyl-*bb*-diphenylthiocarbamide and the action of caustic alkali and of heat on, 74.

Acetylene, thermal decomposition of, 167.

Acetylenedicarboxylic acid, alkaloidal salts, and their optical activity, 61.

Acetylenic acids, formation of 4-pyrone compounds from, 177.

Acetylketen and its phenylhydrazone-phenylhydrazide, 100.

Acetylsalicylic acid, brucine and cinchonine salts, and their optical activity, 186.

Acid, $C_9H_{14}O_4$, from the oxidation of 1:1:5-trimethyl-Δ^4-*cyclo*hexenone-3, 130.

$C_{10}H_{14}O_2$, and its silver salt, from pinene, 31.

$C_{10}H_{16}O_2$, and its chloride, and their bromo-derivatives, from pinene, 31.

$C_{23}H_{46}O_2$, from olive leaves, 117.

$C_{25}H_{46}O_2$, and its ethyl ester, from olive bark, 117.

$C_{26}H_{44}O_4$, and its silver salt, from the oxidation of cholesterol, 121.

$C_{27}H_{42}O_3$, and its dimethyl ester and its oxime from dehydrositostanedione, 228.

$C_{27}H_{46}O_3$, and its ethyl ester and acetyl derivative, from the oxidation of cholesterol, 121.

$C_{30}H_{58}O_2$, and its ethyl ester, from olive bark, 118.

$C_{35}H_{68}O_2$, and its ethyl ester and salts, from olive bark, 117.

$C_{38}H_{76}O_2$, and its ethyl ester and salts, from olive bark, 118.

Acids, modification of the theory of, 274.

containing adjacent unsaturated groups, optically active salts of, 186.

normal fatty, esterification constants of, 14.

melting point of anilides, *p*-toluidides, and *a*-naphthalides of, 120.

organic, salts, the electrolytic chlorination of, 174.

saturated or unsaturated, alkaloid salts, relation between optical activity and unsaturation in, 61.

unsaturated, of the benzene series, relation between the absorption spectra and chemical constitution of, 207.

Acridines, complex, synthesis of, 200.
Acylhydroxyamines, labile isomerism among, 78.
Acylsalicylamides, labile isomerism among, 78.
Adipic acid, *meso*-*aa'*-*di*hydroxy-, preparation of, and action of heat on, and its methyl ester, amide, anilide, and lactone-lactide, 70.
r-*aa'*-*di*hydroxy-, preparation of, and action of heat on, and resolution of its amide, anilide, and dilactone, 70.
Affinity, Chemical :—
Affinity of certain alkaloids for hydrochloric acid, 234.
residual, of the coumarins and thiocoumarins as shown by their additive compounds, 26.
Affinity constants of bases as determined by the aid of methyl-orange, 50, 238.
Affinity values of tropine and its derivatives, 280.
Catalysis, examination of the conception of hydrogen ions in, 275.
Chemical change, homogeneous, in a gas, measurement of a, 190.
dissociation of the polyiodides of the alkali metals and ammonium radicles, 181.
dynamics of the reactions between sodium thiosulphate and organic halogen compounds, 286
Dynamic isomerism, benzylsulphoxide as a possible example of, 285.
Velocity of chemical change, determination of the, by measurement of the gases evolved, 29, 282.
Velocity of change in solid alloys, method for the measurement of, 145.
Velocity of hydrolysis of chloroacetates, bromoacetates, and α-chlorohydrin by water and by alkali, and the influence of neutral salts on the reaction velocities, 89.
Alcohol, $C_9H_{16}O$, and its phenylurethane and acid phthalic ester, from pinene, 31.
$C_{35}H_{68}O$, from olive bark, 118.
Alkali metals, polyiodides of, chemical dissociation of, 181.
polyiodides of, electrolytic dissociation of, 213.
nitrates, spontaneous crystallisation of solutions of, 196.
trithionates and tetrathionates, 199.
Alkalis, action of, on sodium alkyl thiosulphates, 179, 185.
Alkaloids, affinity of certain, for hydrochloric acid, 234.
Alkyl haloids, interaction of, with aluminium, 194.
direct interaction of, with magnesium, 194.
sodium thiosulphates, action of alkalis on, 179, 185.
Alkylsulphine perbromides and periodides, 191.
Alloys, method for the measurement of rate of change in solid, 145.
Allylazoimide and its dibromide and diazoamino-compound, 143.
Aluminium, interaction of, with alkyl haloids, 194.
Aluminium carbide, formation of, 240.
hydroxide, amphoteric character of, 15.
Amides, molecular complexity of, in various solvents, 98.
Amidines, the chemistry of the, 136,
Amine, $C_9H_{17}N$, and its hydrochloride and platinichloride, from pinene, 31,
Amines, interaction of, with 2 : 3 : 5-trinitro-4-acetylaminophenol, 197.
fatty, affinity constants of, as determined by the aid of methyl-orange, 56.
primary, compounds of, with cobaltinitrites, 212.
Amino-aldehydes and amino-ketones of the aromatic series, relation between the absorption spectra and chemical constitution of, 235.
Aminoalkyl esters, relation between chemical constitution and physiological action in certain substituted, 208.
Aminocarboxylic acids, affinity constants of, as determined by the aid of methyl-orange, 50.
Amino-groups, acids as accelerators in the acetylation of, 132.
Amino-ketones and amino-aldehydes, relation between the absorption spectra and chemical constitution of, 235.
Ammonia, chemical action of radium emanation on, 132.
Ammonium chromate, dichromate, and trichromate, slow decomposition of, by heat, 136.
*di*chromate, decomposition of, by heat, 27.
Ammonium cyanate and carbamide, isomerism of, 135
thiocyanate and thiocarbamide, isomerism of, 135.
Ammonium compounds, optically active, effect of constitution on the rotatory power of, 28.
Ammonium radicles, chemical dissociation of polyiodides of, 181.
electrolytic dissociation of polyiodides of, 213.

Amygdalin, hydrolysis of, by emulsin, 97, 181.
l-Amyl alcohol, sulphur derivatives of, and their optical activity, 195.
*iso*Amyl arsenite, 150.
Analysis, new form of potash bulb for, 182.
electrolytic, rapid, of metals, 189.
Anhydrobrazilinic acid, synthesis of, 54.
Anilides, *p*-toluidides, and α-naphthalides of normal fatty acids, melting points of, 120.
Aniline, di-*o*-substituted, preparation of monoacetyl derivatives of, 132.
picrate, *m*-nitro-, 242.
styphnate, *m*-nitro-, 241.
p-nitro-, chlorination of, 211.
Anilinobenzoxazole and its acetyl derivative, 136.
Anisoin, alkylation of, 191.
Annual General Meeting, 81.
Anthracene, oxidation of, 195.
Anthranilic acid, brucine and cinchonine salts, and their optical activity, 186.
Anthraquinones, researches on the, 52.
Antimony, the electroanalytical deposition of, 189.
Apocynin (*acetovanillone*), isolation and constitution of, and its derivatives, 171.
new synthesis of, and its benzoyl derivative, 171.
Apocynol and its benzoyl derivative, 171.
Apocynum cannabinum, constituents of, 171.
Arsenic :—
Arsenious acid, esters, 150.
Arsenious hydroxide, amphoteric character of, 15.
Arsenic organic compounds, 268.
Arsinic acids, aromatic, 143.
Arsonic acids, aromatic, 143.
and their physiological action, 229.
Arylsulphonylbenzidines and their diazonium salts, 51.
Aspartic acid, condensation of, with aminopinenedicarboxylic acid, 144.
Atomic weights, report of the International Committee on, 2.
table of, 5.
relative, of chlorine and hydrogen, 215.
Azo-compounds, constitution and colour of, 6.
Azo-compounds, hydroxy-, constitution of, and the action of diazomethane and of mercuric acetate on, 70.
Azo-compounds, *p*-hydroxy-, salts of, with acids, colour and constitution of, 6.
Azomethine compounds, colour and constitution of, 24, 228.
Azoxybenzene, products of, reduction of, 211.

Barbituric acid, derivatives, replacement of halogen by hydrogen in, 288.
Barium nitrite, molecular volumes of, 240.
Bases, affinity constants of, as determined by the aid of methyl-orange, 50, 238.
Benzaldehyde, *o*-, *m*-, and *p*-chloro-, and *m*- and *p*-nitro-, semicarbazones of, 195.
*di*hydroxy-, methyl ether of, and its oxime, phenylhydrazone, and sodium derivative from the root of a species of Chlorocodon, 62.
Benz*syn*aldoxime, *p*-iodo-, velocity of rearrangement of, in *n*-propyl tartrate, 135.
Benzamide, condensation of, with salicylaldehyde, 229.
Benzene, bromonitroamino-derivatives, the wandering of bromine in, and their reduction, 62.
2:4- and 2:6-*di*bromo-1-nitroamino-, preparation and transformation of, and their barium salts, 62.
Benzeneazo-*p*-cresol, mercuri-acetate and -chloride, 71.
Benzeneazo-3-hydroxypyridine, 174.
Benzeneazo-α-naphthols, α- and β-, action of diazomethane on, 71.
Benzeneazophenol and its bromo-derivatives, mercuri-salts of, 71.
5-Benzeneazo-2-pyridone, synthesis and reduction of, and its chloro-derivative, 174.
Benzil (*dibenzoyl*), 3:4:3′:4′-*tetra*hydroxy-, and its tetrabenzoyl derivative, 60.
Benzoic acid, hydroxy-derivatives, electrolytic oxidation of, 149.
Benzoin, alkylation of, 191.
condensation of, with methyl alcohol, 119.
l-Benzoin, preparation of, 25.
p-Benzoquinone, constitution of, 285.
absorption spectra of, in a state of vapour and in solution, 284.
Benzoylacetylacetone and the action of phenylhydrazine on, 178.
Benzoylanthranilic acid, brucine and cinchonine salts, and their optical activity, 186.

5-Benzoyl-1:3-diphenylbarbituric acid, 5-bromo-, preparation of, and the estimation of bromine in, 288.
a-Benzoyl-*bb*-diphenylthiocarbamide, 74.
Benzoyloxydiphenylamine, bromo-derivatives, 27.
Benzoyloxyethylamine, *p*-amino-, and its hydrochloride, picrate, and dibenzoyl derivative, 227.
β-Benzoyloxy-*β*-3:4-methylenedioxyphenylethyldimethylamine and its additive salts and physiological action, 208.
Benzoylsalicylic acid, brucine and cinchonine salts, and their optical activity, 186.
Benzoylthiocarbimide and its reactions, 74.
Benzyl arsenite, 151.
bromide, *p*-nitro-, interaction of, with *iso*nitrosocamphor in presence of silver oxide, 9.
chloride, *p*-nitro-, interaction of, with *iso*nitrosocamphor in presence of sodium ethoxide, 8.
sodium thiosulphates, *o*-, *m*-, and *p*-nitro-, and the action of alkalis on, 185.
sulphoxide, a possible example of dynamic isomerism, 285.
Benzylethyl*iso*butylsilicol and its chloride and oxide, synthesis of, 224.
Benzylethyldipropylsilicane and its sulphonation, 12.
Benzylethylpropylsilicyl oxide and its sulphonation, 12.
Benzylethylsilicone, 25.
Benzylidene-*o*- and -*p*-aminophenols, and *m*- and *p*-nitro-, 24.
Benzylideneaniline, *o*-hydroxy-, and its *m*'- and *p*'-nitro-derivatives, 24.
Benzyl*iso*thioanilidomethanetricarboxylic acid, diethyl ester, 53.
Bis-*p*-acetylaminophenylarsinic acid and its sodium salt, 144.
Bis-2-acetylaminotolyl-5-arsinic acid and its sodium salt, 143.
Bis-*p*-aminophenylarsinic acid and its sodium and barium salts, 144.
Bis-2-aminotolyl-5-arsinic acid and its sodium salt, 143.
Bishydroxypyridylcarbamide, 174.
Bismuth ion, bivalent, existence in aqueous solutions of a, 76.
Bistriazoacetic acid, ethyl ester, 102.
1:2-Bistriazoethane and the action of magnesium phenyl bromide on, 102.
Books, gift of, from Sir Henry E. Roscoe, 278, 289.
Boron thiocyanate, 270.
Brazilein and its derivatives, 148.
Brazilin and hæmatoxylin and their derivatives, 148.
constitution of, 54.
Brazilinic acid, synthesis of, 54.
Bromides, delicate test for, alone or in solution with chlorides, 144.
Burette, gas, new form of, 210.
Burettes, gas, a combined stopcock and capillary connecting tube for, 95.
Butanone-2 (*methyl ethyl ketone*), azoimides of, 54.
*iso*Butyl arsenite, 150.

Cadmium ion, univalent, existence in aqueous solutions of a, 76.
Cæsium nitrate, crystallisation of, 196.
trithionate and its monohydrate, 199.
Cæsium and rubidium, estimation of, 200.
Calcium carbonate, polymorphism of, 193.
nitrite, molecular volumes of, 240.
oxide (*lime*), solubility of, in water, 202.
Camphor, absorption spectrum of, 120.
mercury derivatives, 267.
double salts of, with potassium iodide and mercuric iodide, 266.
Camphor, imino-, action of formaldehyde on, 9.
*iso*nitroso-, action of diazomethane on the two modifications of, 8.
interaction of, with *p*-nitrobenzyl bromide and chloride, 8.
N-ethyl ether of, 9.
d-Camphor, sulphur derivatives of, and their rotatory power, 195.
Camphorquinone, action of hydrogen peroxide on, 9.
Carbamide and ammonium cyanate, isomerism of, 135.
Carbides, formation of some, 240.
Carbon, apparatus for experiments at high temperatures and pressures on, 131.
direct union of, with hydrogen, 222.
reducibility of magnesium oxide by, 29.
Carbon oxides, chemical action of radium emanation on, 132.
*di*oxide, decomposition of, by the silent electric discharge, 271.
α-3:4-Carbonyldioxyphenylethane, *αβ*-dichloro-, 237.
α-3:4-Carbonyldioxyphenylpropane, *αβ*-*di*chloro-, 237.
Carboxyethylthiocarbimide and the action of diphenylamine on, 74.
α-Carboxymethyl-*ab*-diphenylthiocarbamide, preparation of, 74.
Carboxymethylthiocarbimide and the action of diphenylamine on, 74.

*iso*Carvestrene ($\Delta^{6,8(9)}$-m-*menthadiene*), synthesis of, 228.
Catechol, reaction of diazonium salts with, 118.
derivatives, methylene ethers, action of phosphorus pentachloride on, 237.
action of thionyl chloride and of phosphorus pentachloride on, 50.
action of thionyl chloride on, 60.
Chemical constitution and absorption spectra, relation between, 173, 207, 223, 235, 268.
relation of, to colour and fluorescence, 204.
and colour of azomethine compounds, 24, 228.
and dielectric constant, relation between, 124.
and physiological action, relation between, in certain substituted aminoalkyl esters, 208.
and viscosity, relation between, 213, 224.
effect of, on the optical activity of nitrogen compounds, 148.
effect of, on the rotatory power of optically active ammonium compounds, 28.
effect of, on the rotatory power of optically active nitrogen compounds, 212.
Chlorination, electrolytic, of the salts of organic acids, 174.
Chlorine and hydrogen, relative atomic weights of, 215.
Chlorocodon from Uganda, a new isomeride of vanillin from, 62.
α-Chlorohydrin, rate of hydrolysis of, by water and by alkali, and the influence of neutral salts on the reaction velocity, 89.
Cholestenone and its ozonide, 173.
Cholesterol, action of fused potassium hydroxide and of hydrogen peroxide on, 121.
ozonide of, 173.
Cholesterol group, contributions to the chemistry of the, 121, 227.
Chromium *sesqui*oxide, reduction of, by carbon, 188.
Chromous chloride, preparation of pure, and its hydrates, 215.
Cinnamic acid, alkaloidal salts, and their optical activity, 61.
Cinnamic acid, menthyl ester, optical rotatory power of, 286.
Cobaltinitrites, studies on the, 212.
Colloidal solutions, viscosity of, 121.
Colour and constitution of azomethine compounds, 24, 288.
Colour and fluorescence, relation of, to constitution, 204.
in the triphenylmethane series, cause of, 206.
Colouring matters of the stilbene group, 201.
Co-ordinated compounds, constitution of, 94.
Copper, interaction of, with nitric acid in presence of metallic nitrates, 141.
direct action of radium on, 214.
Coprostanone and its oxime, semicarbazone, and phenylhydrazine compound, 196.
Coprosterol, 196.
ψ-Coprosterol and its acetate and benzoate, 196.
Coumarin and thio-, and their mercurichlorides, 26.
Coumarins and thio-, residual affinity of, as shown by their additive compounds, 26.
formation of, 229.
o-Cresol, 3-bromo-, 3-bromo-5-nitro-, and its potassium salts, and 5-bromo-3-nitro-, potassium salts of, 73.
p-Cresol, condensation of, with epichlorohydrin, 92.
Crystal form of halogen derivatives of open-chain hydrocarbons with reference to the Barlow-Pope theory of structure, 29.
Crystallisation, spontaneous, the temperatures of, of mixed solutions and their determination by means of the index of refraction, 30.
of solutions of some alkali nitrates, 196.
of substances which form a continuous series of mixed crystals, 125.
*iso*Cyanine dyes, optical and sensitising properties of, 134.

Datura Meteloides, meteloidine from, 234.
Dehydrocholestanedionol (*oxycholestenediol*), formation of, 121.
Dehydrositostanedionol, Dehydrositostenedione and its phenylhydrazone, and Dehydrositostanedione and its dioxime, 227.
Dehydrositostanetriol and its acyl derivatives, 227.
Density, apparatus for determining the. See Pyknometer.
of solids, use of the micro-balance for the measurement of, 185.
Dextrose derivatives, constitution of, 186.
Diacetanilides, formation of, 132.

Diamond, summary of information as to the artificial production of, 131.
Di*iso*amylsulphoxide, preparation of, 216.
Diazobenzene (*benzenediazonium*) chloride, rate of decomposition of, 252.
p-Diazoiminobenzene, derivatives of, 48.
Diazomethane, action of, on the two modifications of *iso*nitrosocamphor, 8.
action of, on hydroxyazo-compounds, 70.
Diazonium bromides, new general method of preparing, 93.
*per*bromides, constitution of, 172.
salts, quantitative conversion of aromatic hydrazines into, 74.
reaction of, with mono- and dihydric phenols and with naphthols, 118.
Diazo-reaction, study of, in the diphenyl series, 51.
αβ-Dibenzoyl-α-methoxydibenzyl and its reactions, 119.
s-Di-β-benzoyloxy-1:4-diethylpiperazine and its additive salts and physiological action, 208.
βγ-Dibenzoyloxydiethylpropylamine and its additive salts and physiological action, 208.
βγ - Dibenzoyloxydimethylpropylamine and its additive salts and physiological action, 208.
s- ββ - Dibenzoyloxymethyldiethylamine and its additive salts and physiological action, 208.
βγ - Dibenzoyloxy -1 - propylpiperidine and its additive salts and physiological action, 208.
s-ββ-Dibenzoyloxytriethylamine and its additive salts and physiological action, 208.
Dibenzyl diselenide, 134.
sulphoxide, preparation of, 216.
Dibenzylethyl-silicol and -silicyl oxide, 25.
Dibenzylsilicols, α- and β-, 25.
Dibenzylsilicon dichloride, 25.
Dibenzylsilicone and its termolecular compound, 25.
Dicamphorylarsinic acid and its cadmium and silver salts and chloride, 268.
Dicholesteryl ether, oxidation of, 121.
1:4-Diethanolpiperazine and its additive salts, 208.
4:4′-Diethoxydiphenyl sulphoxide, preparation of, 216.
Diethoxypyridine, *di*bromo- and *di*chloro-, 225.
Diethylaminoethyl phthalate and its additive salts, 208.
Diethyl ketone, reaction of, with mercuric iodide in alkaline solution, 267.
Diglycollic acid, *di*thio-, and its esters, 198.
Dihydrobenzenes, substituted, 59.
Dihydrobrazilinic acid, lactone of, synthesis of, 54.
Dihydro*iso*carvestrenol (Δ⁶-m-*menthenol*-(8)) and its nitrosochloride, synthesis of, 228.
Dihydrodi*cyclo*pentadiene, nitro-, nitrite of, nitrohydroxy-, and its sodium salt and ψ-nitrol, and nitro*iso*nitroso-, 175.
Dihydrohæmatoxylinic acid, lactone of, synthesis of, 54.
Dilactylic acid, α- and β-*di*thio-, and their esters, 198.
Dimethoxyanthraquinone, *tri*hydroxy-, 52.
o-Dimethoxybenzoin, alkylation of, 192.
2:2′-Dimethoxystilbene, 4:4′-*di*nitro-, 202.
3:5 - Dimethoxytetra-anisyltetrahydrofuran, 2-hydroxy-, 192.
3:5 - Dimethoxytetraphenyltetrahydrofuran, 2-hydroxy-, and its triacetyl derivative, 119.
Dimethylaminobenzeneazo - α - naphthol and its hydrochlorides, platinichloride, methiodide, acetyl and benzoyl derivatives, and ethyl ether and its dihydrochloride and platinichlorides, 6.
4:7-Dimethylcoumarin and its additive salts, oxime, and phenylhydrazone, 26
1:1-Dimethyl-Δ^{2,4}-dihydrobenzene and Δ^{2,5}-dihydrobenzene, 59.
Dimethylethyl*cyclo*hexenone, synthesis of, 281.
1:1-Dimethyl-Δ⁴-*cyclo*hexen - 3 - one-5-acetic acid, ethyl ester, and its semicarbazone, 130.
ββ-Dimethylpropane, *tetra*bromo-, crystal form of, 29.
Dimethylpropyl*cyclo*hexenone, synthesis of, 281.
1:1-Dimethyl- 5 - propyl - Δ⁴ - *cyclo*hexen-one-3 and its semicarbazone, 130.
2:2-Dimethylstilbene, 4′:4′-*di*nitro-, 202.
4:7-Dimethylthiocoumarin and its mercurichloride, 26.
ββ-Dinaphthyl, absorption spectra of, 147.
Di-*o*-, -*m*-, and -*p*-nitrobenzyl disulphides, preparation of, 185.
Di*cyclo*pentadiene, action of nitrous gas on, 175.
Diphenanthracridine, preparation of, 200.
Di-*p*-phenetyl-α-disulphone, 192.
Diphenyl sulphoxide, 4:4′-*di*amino-, preparation of, 216.

Diphenylamine sulphoxide, *isodi*nitro-, derivatives of, 199.
Diphenylamine, *p*-hydroxy-, bromination of, 27.
Diphenylamine-*o*-sulphonic acids, *di*nitro-, and their salts, 147.
s-Diphenylcarbamide and its *p-mono*-, *di-p*-, and *tri*-chloro-derivatives, 136.
Diphenyl-α-disulphone, 192.
Diphenylothylsilicyl chloride and oxide, 12.
Diphenylmethane, oxidation of, 195.
2:6-Diphenyl-4-pyrone and its platinichloride, 52.
Diphenyl series, study of the diazo-reaction in the, 51.
1:3-Diphenyl-2-thiobarbituric acid, 5-*mono*- and -*di*-bromo-, preparation of, and the estimation of bromine in, 288.
Diselenides, preparation of, 134.
Distillation, vacuum, a simple manometer for, 51.
Disulphides, preparation of, 179, 185, 198.
α-Disulphones, aromatic, 192.
s-Di-*p*-tolylcarbamide, 136.
Di-*p*-tolyl-α-disulphone, 192.
Dixanthyl derivatives, new, 205.
Di-*p*-xylyl-α-disulphone, 192.

Egg-yolk, the proteins of, 190.
ELECTROCHEMISTRY :—
Electrochemical equivalents, use of the micro-balance for the determination of, 185.
Dielectric constant and chemical constitution, relation between, 124.
apparatus for determining the, of organic liquids, 124.
Electrode, hydrogen, anomalous behaviour of the, in solutions of lead salts, 14.
Electrolytic conduction, examination of the conception of hydrogen ions in, 275.
dissociation of the polyiodides of the alkali metals and ammonium radicles, 213.
conductivity and viscosity of aqueous solutions, 187.
Electron, the, as an element, 87.
Ionic mobility, elucidation of the connexion between, and the fluidity of the solution, 187.
Element, new tin-group, in thorianite, 60.
Emulsin, hydrolysis of amygdalin by, 97, 181.
Epichlorohydrin, condensation of, with phenols, 92.
Ester catalysis, 274.
Ester hydrolysis, 152.
Esterification, theories of, 152.
Esterification constants of the normal fatty acids, 14.
Esters, formation and hydrolysis of, 153.
Ethane, thermal decomposition of, 167.
bistriazo-derivative of, 102.
Ethers, formation of, from compounds of the benzoin type, 191.
Ethoxide, lead, formation of, 179.
2-Ethoxyindene, 3-cyano-, formation of, 13.
Ethylcatechol, *di*chloro-, cyclic carbonates of, 237.
Ethylene, thermal decomposition of, 167.
Ethylene, *tetra*iodo-, crystal form of, 29.

Fenchone, comparison of, with α-methyl camphor, 151.
Fermentation, studies in, 11.
alcoholic, the mechanism of, 11.
Ferro-alloys, production of, 189.
Fluorene, oxidation of, 195.
Fluorene, 2-amino-, and its reactions, 200.
Fluorene-N—α / CH—β -naphthacridine, preparation of, 200.
Fluorescence and colour, relation of, to constitution, 204.
of platinocyanides, 178.
Formic acid, ethyl ester, saponification of, by water in presence of acids as catalytic agents, 100.
Fumaric acid, alkaloidal salts, and their optical activity, 61.
Furoin, alkylation of, 192.

Gallic acid, electrolytic oxidation of, 149.
action of reducing agents on, 272.
Gas, measurement of a homogeneous chemical change in a, 190.
Glucose-anilide, preparation, alkylation, and mutarotation of, 186.
Glucosehydrazone, constitution of, 186.
Glucoseoxime, preparation and alkylation of, 186.
Glyceryl diphenyl ether, 92.
di-*p*-tolyl ether, 92.
Glycine (*aminoacetic acid*), condensation of, with aminopinenedicarboxylic acid, 144.
Gold, direct action of radium on, 214.
Guaiacol, *o*- and *p*-bromo-, and 6-bromo-4-nitro-, and its potassium salts and 4-bromo-6-nitro-, potassium salts of, 73.

Hæmatein and its derivatives, 148.
Hæmatoxylin and brazilin and their derivatives, 148.
constitution of, 54.
Halogen carriers, use of pyridine bases as, 15.
Halogen compounds, organic, interaction of, with aluminium, indium, and thallium, 194.
the chemical dynamics of the reactions between sodium thiosulphate and, 286.
$\Delta^{1:3:5}$-Hexatriene *di-* and *tetra*-bromides, crystal form of, 21.
Homo-olestranol, 117.
Hydrazines, aromatic, oxidation of, by metallic oxides, permanganates, and chromates, 10.
conversion of, into diazonium salts, 74.
Hydrindene derivatives, formation of, from *o*-phenylenediacetonitrile, 12.
Hydrindene, β-imino-α-cyano-, and its phenylhydrazine derivative, 12.
β-Hydrindone, preparation of, 13.
action of bromine on, 192.
β-Hydrindone, α-cyano-, and its phenylhydrazone, metallic salts, and *O*-benzoyl derivative, 13.
Hydrocarbons, formation of, by the interaction of metals of the aluminium group with organic haloids, 194.
formation of, by the interaction of alkyl haloids with magnesium, 194.
thermal decomposition of, 167.
aromatic, relation between the absorption spectra and chemical constitution of, 223.
of the benzene series, oxidation of, 195.
open-chain, halogen derivatives, crystal form of, with reference to the Barlow-Pope theory of structure, 29.
Hydrogen and chlorine, relative atomic weights of, 215.
passage of, through a palladium septum, and the pressure it produces, 208.
direct union of, with carbon, 222.
and nitrogen, chemical action of radium emanation on, 132.
and oxygen, chemical action of radium emanation on, 132.
Hydrogen chloride (*hydrochloric acid*), conductivity and viscosity of solutions of, 187.
chemical action of radium emanation on, 132.
*di*oxide, interaction of, with sulphides, 216.
Hydrogen ions, examination of the conception of, in catalysis, salt formation, and electrolytic conduction, 275.
Hydropiperoin and *iso*Hydropiperoin, action of thionyl chloride on, 60.
Hydroxy-acid, $C_{10}H_{16}O_2$, and its salts, from pinene, 31.
α-Hydroxycarboxylic acids, action of heat on, 70.

Iminazoles, formation of, 197.
Imino-compounds, formation and reactions of, 12, 283.
Indene-3-carboxylic acid, 2-amino-, and its ethyl ester and amide and their hydrochlorides, 13.
Indium, interaction of, with organic halogen compounds, 194.
Intramolecular rearrangement in inactive substances, polarimetric study of, 135.
Iodine, liberation of, from hydriodic acid by certain halogenated malonyl derivatives, 288.
solubility of, in water, 58.
reaction of, with phosphorous acid, 193.
Ipuranol and its diacetyl derivative from olive bark, 118.
Iron, the rusting of, 169.
rust, composition of, 169.
Iron carbide, formation of, 241.

Keten, some reactions of, 77.
polymeride of, 100.
Keto-alcohol, $C_{27}H_{44}O_3$, and its acetate and phenylhydrazone, from the oxidation of the substance, $C_{27}H_{46}O_3$, from cholesterol, 121.
Ketone, $C_9H_{14}O$, from pinene, 31.
Ketones, condensation of, with ethyl phenylpropiolate, 52.
action of mercuric iodide on, in alkaline solution, 266.
hydroaromatic, 130, 281.
Ketonic acid, $C_{26}H_{42}O_3$, and its oxime and potassium salt, from cholestenone, 173.
4-Keto-2-phenyliminotetrahydrothiophen-3-dicarboxylic acid, ether ester, and its isomeride, 53.
Krypton, density of, 272.

Lævulose, fermentation of, by yeast juice, 115.
Lead potassium *per*iodide, Wells', composition and formula of, 97.
nitrate and sodium nitrate, temperatures of spontaneous crystallisation of mixtures of, 30.
potassium nitrites, complex, 97.
Lead ions, univalent, existence of, in aqueous solutions, 14.

Lithium chloride, conductivity and viscosity of solutions of, 187.
and sucrose, conductivity and viscosity of mixtures of solutions of, 187.
nitrite and its decomposition by heat, 75.
molecular volume of, 75.
Livetin from egg-yolk, 190.

Magnesium, direct interaction of, with alkyl haloids, 194.
Magnesium carbide, formation of, 241.
oxide, reducibility of, by carbon, 29.
Malacone, a silicate of zirconium, 28.
Maleic acid, alkaloidal salts, and their optical activity, 61.
Malonic acid, ethyl ester, action of phenolthiocarbimide on, 53.
action of monochloromethyl ether on, 212.
action of ethyl chloroacetate on, 53.
Malonyl derivatives, liberation of iodine from hydriodic acid by certain halogenated, 288.
Malonyldiurethane, bromo-, preparation of, and the estimation of bromine in, 288.
Mandelonitrile glucoside, Fischer's, formation of, 182.
Manganous oxide, reduction of, by carbon, 188.
Mannose, fermentation of, by yeast-juice, 115.
Manometer, simple, for vacuum distillation, 51.
Mellitic acid (*benzenehexacarboxylic acid*), constitution of the phthaleins of, 209.
Mellitic acid, rhodamines of, 204.
Melting points of the anilides, *p*-toluidides, and α-naphthalides of the normal fatty acids, 120.
Menthols, isomeric, and their acid esters, 217.
Mercury iodide, condensation of, with camphor, 267.
Mercuric iodide, action of, on ketones in alkaline solution, 266.
double salt of, with potassium iodide in organic solvents, 266.
nitrate solution, solubility of silver chloride in, 173.
Mercuric zinc cyanide, formula of, 135.
Mercurous nitrite, molecular volume of, 75.
Metallic cyanides, reactions of, with phenylhydrazine, 179.
hydroxides, amphoteric, 15.
Metallic oxides, reduction of, by carbon, in presence of metallic iron and other substances, 189.
refractory, reduction of, by carbon, 188.
salts, fused, viscosity of, at high temperatures, 146.
reactions of, with phenylhydrazine, 179.
Metals, the rapid electro-analytical deposition and separation of, 189.
viscosity of, 146.
Meteloidine from *Datura Meteloides* and its additive salts, 234.
Methane, synthesis of, 222.
thermal decomposition of, 167.
Methanesulphonic acid, chlorobromo-, strychnine and quinidine salts, and their optical activity, 99.
Methanetricarboxylic acid, thioanilide and thioallylamide, diethyl esters and diamides of, 53.
diethyl ester, thioanilide of, action of ethyl chloroacetate on, 53.
Methoxyanthraquinone, *di*hydroxy-, 52.
Methoxydihydrodi*cyclo*pentadiene, nitro-, 175.
2-Methoxyindene, 3-cyano-, 13.
β-Methoxymethylmalonic acid, ethyl ester, synthesis and reactions of, 212.
β-Methoxymethyl-β-*iso*propylmalonic acid and its ethyl ester and barium salt, synthesis of, 212.
Methyl alcohol, condensation of, with benzoin, 119.
Methyl ether, *mono*chloro-, syntheses with, 212.
Methylcampholenitrile, 152.
α-Methylcamphor, preparation of, and its bromo-derivatives and β-sulphonic acid and its derivatives, and oxime, 151.
comparison of, with fenchone, 151.
7-Methylcoumarin and its additive salts, oxime, and phenylhydrazone, 26.
α-3 : 4-Methylenedioxyphenylethane, αβ-*di*chloro-, αβ-ω-ω-*tetra*chloro-, and β-chloro-α-hydroxy-, 237.
β-3 : 4-Methylenedioxyphenylethyldimethylamine, β-hydroxy-, and its benzoyl derivative and their additive salts, 208.
α-3 : 4-Methylenedioxyphenylpropane, αβ-ωω-*tetra*chloro-, 237.
1-Methyl*cyclo*hexan-2-ol-4-carboxylic acids, *cis*- and *trans*-, and their conversion into 1-methyl-Δ¹-*cyclo*hexene-4-carboxylic acid, 187.
1-Methyl-Δ³-*cyclo*hexene-4-acetic acid and its ethyl ester and nitrile ester, 230.

1-Methyl-Δ^6-*cyclo*hexene-3-carboxylic acid and its calcium salt and ethyl ester, synthesis of, 228.
1-Methyl-Δ^1-*cyclo*hexene-4-carboxylic acid, formation of, from *cis*- and *trans*-1-methyl*cyclo*hexan-2-ol-4-carboxylic acids, 107.
dl-1-Methyl-Δ^1-*cyclo*hexene-4-carboxylic acid, resolution of, 228.
1-Methyl*cyclo*hexylidene-4-acetic acid, experiments on the synthesis of, and its ethyl ester, 145, 230.
α-Methyl-β-hydrindone, α-cyano-, and its phenylhydrazone, 13.
Methyloleanol and its acetyl derivative, 117.
2-Methylpiperidine and water, mutual solubility of, 119.
Methyl*iso*propyl*cyclo*pentanes, synthesis of terpins, terpineols, and terpenes from, 64.
2-Methylpyridine (*α-picoline*), chlorination of, 225.
2-Methylpyridine-3 : 5-dicarboxylic acid, 6-hydroxy-, and its salts, 136.
ethyl ammonium and ethyl-silver ester salts, 136.
6-Methyl-2-pyrone-3 : 5-dicarboxylic acid, ethyl ester, and its derivatives and reactions, 136.
7-Methylthiocoumarin, 26.
Micro-balance, use of, for the determination of electrochemical equivalents and for the measurements of densities of solids, 185.
Molecular complexity of amides in various solvents, 98.
conductivities of α-oximino-fatty acids, 191.
Morindin and its acetyl derivative, 149.

Naphthalene and its derivative, absorption spectra of, 223.
and β-naphthol, crystals of, and of their mixtures, 125.
oxidation of, 195.
absorption spectra of the hydrocarbons isolated from the products of the action of aluminium chloride on, 147.
styphnate, α-bromo-, 241.
α-Naphthalides, anilides, and *p*-toluidides of normal fatty acids, melting points of, 120.
β-Naphthol and naphthalene, crystals of, and of their mixtures, 125.
molecular compound of, with 2 : 3 : 5-trinitro-4-acetylaminophenol, 210.
Naphthols, reaction of, with diazonium salts, 118.
Naphthyl arsenite, 151.
1 : 3-Naphthylenediamine, formation of, from β-imino-α-cyano-γ-phenylpropane, 283.
Nicotinamide, 6-chloro-, 174.
Nicotinic acid, hydroxy-, ethyl ester, azide, and hydrazide of, 174.
Nitro-compounds, relation between the absorption spectra and chemical constitution of, 173.
Nitrogen and hydrogen, chemical action of radium emanation on, 132.
Nitric acid, interaction of, with copper in presence of metallic nitrates, 141.
Hyponitrous acid, decomposition of, 16.
Nitrogen compounds, effect of constitution on the optical activity of, 148.
optically active, effect of constitution on the rotatory power of, 212.
Nitroso-compounds, relation between the absorption spectra and chemical constitution of, 173.
Nucleoprotein, reaction distinguishing phosphoprotein from, 200.
Nutmeg, constituents of the expressed oil of, 197.

Ocimum viride, oil from the leaves of, 63.
Oleanol and its mono- and di-acetyl derivatives, 117.
Oleasterol, 117.
Olenitol and its acetyl derivative, 118.
Olestranol and its acetate and benzoate, 117.
Olive bark, constituents of, 117.
Olive leaves, constituents of, 117.
Orcinol, azo-derivatives of, 118.
Origanene and its derivatives from Cyprus origanum oil, 91.
Origanum oil from Cyprus, constituents of, 91.
α-Osazones, stereoisomeric, an alternative structure for the supposed, 175.
Oxalic acid, ammonium, thorium, and uranium salt, 61.
Oxalyl chloride, 271.
α-Oximinobutyric acid, two forms of, 191.
α-Oximino-fatty acids, conductivities of the, 191.
α-Oximinovaleric acid, two forms of, 191.
Oxygen and hydrogen, chemical action of radium emanation on, 132.
Ozone, thermal decomposition of, 190.

α-4 : 4′ : 4″ : 4‴-Pentamethoxy-αβ-dibenzoyldibenzyl, 192.
Perhalogen salts, studies of the, 191.
Phenanthrene styphnate, 241.

Phenol, condensation of, with epichlorohydrin, 92.
derivatives containing a mobile nitro-group, syntheses with, 197.
2:3:5-*tri*nitro-4-amino-, *N*-acetyl derivative of, interaction of, with amines, 197.
molecular compound of, with β-naphthol, 210.
Phenolic ethers sulphination of, and the influence of substituents, 61.
Phenols, reaction of, with diazonium salts, 118,
action of iodine on, 273.
Phenophenanthracridine, preparation of, 200.
Phenoxy*di*chloropropane, 92.
Phenoxydiphenetylsulphonium salts, 123.
Phenoxydiphenylsulphonium salts, 124.
Phenyl arsenite, 150.
glycide ether and its reactions, 92.
Phenyl-*p*-aminobenzeneazo-β-naphthol and its 2- and 4-mono-, 2:4-di-, and 2:4:6-tri-nitro-derivatives, 48.
Phenylbenzylethylpropylsilicane, sulphonation of, 12.
Phenylbenzylmethylallylammonium salts, *p*-bromo-, optical activity of, 148.
Phenylbenzylmethyl-*n*-butylammonium salts, *p*-bromo-, optical activity of, 148.
γ-Phenylbutyric acid, β-imino-α-cyano-, and its ethyl ester, 283.
r-Phenylchloroacetic acid, resolution of, 91.
l-Phenylchloroacetic acid, displacement of halogen in, by hydroxy- and methoxy-groups, 91.
o-Phenyleneaceticpropionic acid, 13.
Phenylhydrazine, oxidation of, by Caro's acid, 76.
reactions of, with metallic cyanides and salts, 179.
Phenylmethyl-*n*-butylallylammonium salts and *p*-bromo-, optical activity of, 148.
Phenylmethyl-ethyl-, -*n*- and -*iso*-propyl-, -*iso*butyl-, and -*iso*-amyl-allylammonium salts, *p*-bromo-, effect of constitution on the rotatory power of, 28.
2-Phenyl-6-methyl-4-pyridone and its salts, 178.
2-Phenyl-6-methyl-4-pyrone and its platinichloride. 52.
S-Phenylphenazothionium, derivatives of, 199.
Phenyl-*p*-phenylenediamine and 2- and 4-*mono*-, 2:4-*di*-, and 2:4:6-*tri*-nitro-, and their diazo-derivatives, 48.
Phenylpropiolic acid, alkaloidal salts, and their optical activity, 61.
Phenylpropiolic acid, ethyl ester, condensation of, with ketones, 52.
β-Phenylpropionic acid, alkaloidal salts and their optical activity, 61.
γ-Phenylpropane, β-imino-α-cyano-, preparation of, and formation of 1:3-naphthylenediamine from, 283.
Phenylthiocarbimide, action of, on ethyl malonate and on ethyl cyanoacetate, 53.
*iso*Phorone, synthesis of, 281.
Phosphoprotein, reaction distinguishing nucleoprotein from, 200.
Phosphoproteins, distribution of, in tissues, 200.
Phosphorus, atomic volumes of, 214.
Phosphorus *penta*bromide, liquid, specific volumes of, 214.
*penta*chloride, action of, on the methylene ethers of catechol derivatives, 50, 237.
Phosphoric acid, electrical conductivity of, 239.
Phosphorous acid, oxidation of, by iodine, 193.
Phosphorus *tri*rhodanide, 239.
Phosphoryl *tri*rhodanide, 239.
PHOTOCHEMISTRY:—
Polarimetric study of intramolecular rearrangement in inactive substances, 135.
Optical activity and unsaturation, relation between, 61, 186, 195.
of compounds having simple molecular structure, 99.
of nitrogen compounds, effect of constitution on the, 148.
Optical inversion, Walden's, contribution to the chemistry of, 91.
Optically active compounds, influence of solvents on the rotation of, 125, 216.
Dispersion and refraction of triazo-compounds, 114.
Refraction and dispersion of triazo-compounds, 114.
Rotation, influence of temperature change on, in solution, 216.
of optically active compounds, influence of solvents on, 125, 216.
Rotatory power, the relative influence of bi-, quadri- and sexa-valent sulphur on, 195.
of optically active ammonium compounds, effect of constitution on the, 28.
of optically active nitrogen compounds, effect of constitution on the, 212.

PHOTOCHEMISTRY:—
Spectra, absorption, and chemical constitution, relation between, 173, 207, 223, 235, 268.
Phthaleins, constitution of the salts of the, and the cause of the colour in the triphenylmethane series, 206.
Phthaleins of mellitic and pyromellitic acids, constitution of the, 209.
Phthalidecarboxylic acid and its silver salt, formation of, 193,
Physiological action and chemical constitution, relation between, in certain substituted aminoalkyl esters, 208.
Picene, alkyl derivative of, 147.
Picolinic acid, 3:5-*di*chloro-, and its methyl ester and amide, 225.
Picric acid, molecular compounds of, 241.
metallic salts and their hydrates and hydrazine salt, 22.
Pinene, oxidation products of, 31.
Pinenedicarboxylic acid, amino-, condensation of, with aspartic acid and with glycine, 144.
Piperidylethyl benzoate and its additive salts and physiological action, 208.
phthalate and its additive salts, 208.
Piperil, action of thionyl chloride on, 60.
Piperonal*syn*oxime, rate of inversion of, in inactive substances, 135.
Piperonyloin, action of thionyl chloride on, 60.
Platinocyanides, fluorescence of, 178.
Polyiodides, formation of, in nitrobenzene solution, 181, 213.
Polymorphism, 193.
Potash bulb, new form of, 182.
Potassium iodide, double salts of, with mercuric iodide and dimercuriodocamphor in organic solvents, 266.
lead *peri*odide, Wells', composition and formula of, 97.
nitrate, crystallisation of, 196.
nitrite, molecular volume of, 75.
lead nitrites, complex, 97.
sulphite and potassium pentathionate, the reaction between, 122.
*tri*thionate, 199.
Propionic acid, ethyl ester, azoimides of, 54.
Propionitrile, additive compound of, with silicon tetrabromide, 280.
Propyl arsenite, 150.
Propylcatechol, *di*chloro-, cyclic carbonates of, 237.
*iso*Propylmalonic acid, ethyl ester, sodium derivative, action of monochloromethyl ether on, 212.
*iso*Propylmalonic acid, β-hydroxy-, β-lactone of, from acetone and malonic acid, and its salts, 31.
Proteins of egg-yolk, 190.
Protocatechuic acid, electrolytic oxidation of, 149.
Purpurogallincarboxylic acid and its salts and tetramethyl ether and the methyl ester of the ether, 149.
Purpurogallonecarboxylic acid and its acetylation and tetramethyl ether and the methyl ester of the ether, 149.
Pyknometer, new form of, 69.
Pyranol salts related to brazilein and hæmatein, synthesis and constitution of, 148.
Pyridine, some physico-chemical properties of mixtures of water and, 22, 59.
additive compound of, with silicon tetrabromide, 280.
chlorination of methyl derivatives of, 225.
Pyridine, 3:5-*di*chloro-, preparation and orientation of, 225.
2:3:5-*tri*chloro-, orientation of, 225.
2-chloro-5-amino-, 174.
3:5-*di*chloro-2-amino-, formation of, and its platinichloride, and 3:5-*di*chloro-2-hydroxy-, 226.
Pyridine bases, use of, as halogen carriers, 15.
2-Pyridone, 5-amino-, synthesis of, and its *N*-benzoyl derivative, 174.
2-Pyridyl benzoate, 5-amino-, *N*-benzoyl derivative of, 174.
Pyromellitic acid, constitution of the phthaleins of, 209.
4-Pyrone compounds, formation of, from acetylenic acids, 52, 177.
Pyrones and allied compounds, relation between absorption spectra and chemical constitution of, 268.
Pyrrole, potassium derivative, action of silicochloroform on, 279.
silicon compound of, 279.

Quinhydrone, absorption spectra of, in a state of vapour and in solution, 284.
Quinol, absorption spectra of, in a state of vapour and in solution, 284.
reaction of diazonium salts with, 118.
Quinoneanil, bromo-derivatives, 27.

Racemic compounds, existence of, in the liquid state, 213.
Radium, direct action of, on copper and gold, 214.
chemical action of, on water and certain gases, 132.

Radium emanation, the initial change of the, 64.
chemical action of, on water, 133.
Resorcinol, azo-derivatives of, 118.
Rhodanides of inorganic radicles, constitution and properties of, 238.
Rubidium nitrate, crystallisation of, 196.
*tri*thionate, 199.
Rubidium and cæsium, estimation of, 200.

Salicylaldehyde, condensation of, with benzamide, 229.
Salicylic acid, brucine and cinchonine salts, and their optical activity, 186.
Salicylidenebenzamides, isomeric, preparation of, 229.
Salicylidenediamine, di- and tri-benzoyl derivatives of, 229.
Salt formation, examination of the conception of hydrogen ions in, 275.
Salts, complex, constitution of, and a criticism of Werner's theory, 122.
Silicochloroform, action of, on potassium pyrrole, 279.
Silicotetrapyrrole, 279.
Silicon *tetra*bromide, additive compounds with acetonitrile, propionitrile, and pyridine 280.
carbide, formation of, 240.
*di*oxide (*silica*), reduction of, by carbon, 188.
sulphides and oxysulphides, 131.
Silicon organic compounds, 12, 25, 47, 224, 236, 279, 280.
Silver chloride, solubility of, in mercuric nitrate solution, 173.
nitrite, molecular volume of, 75.
Silver, new test for, 125.
estimation of, volumetrically, 122.
Silver, quantitative separation of thallium from, 75.
Sitosterol and its phenylcarbamate and oxidation products, 227.
Sodium nitrate, polymorphism of, 193.
and lead nitrate, the temperature of spontaneous crystallisation of mixtures of, 30.
nitrite, molecular volume of, 75.
sulphate solutions, spontaneous crystallisation of, 70.
thiosulphate, the chemical dynamics of the reactions between organic halogen compounds and, 286.
Sodium alkyl thiosulphates, action of alkalis on, 179, 185.
o-, *m*-, and *p*-nitrobenzyl thiosulphates and the action of alkalis on, 185.
Solutions, viscosity of, 121.
Solutions, viscosity and conductivity of some aqueous, 187.
Solvents, influence of, on the rotation of optically active compounds, 125 216.
Stereoisomeric compounds, relation between dielectric constant and chemical constitution of, 124.
Stilbene, 2 : 4 : 2′ : 4′-*tetra*-amino- and -nitro-, 202.
Stilbene-2 : 2′-dicarboxylic acid, 4 : 4′-*di*nitro-, and its sodium salt, 202.
Stilbene group, colouring matters of the, 201.
Strontium nitrite, molecular volumes of, 240.
Styphnic acid, molecular compounds of, 241.
Styrenes, action of thionyl chloride on, 237.
Substance, $C_{10}H_{16}O$, from the Californian laurel, 24.
$C_{10}H_{13}OBr$, from the acid, $C_{10}H_{15}O_2Br$, from pinene, 31.
$C_{10}H_{15}OCl$, from pinene, 31.
$C_{14}H_{16}N_2$, from the action of magnesium phenyl bromide on bistriazoethane, 102.
$C_{17}H_{18}O_3N_2$, from the interaction of *p*-nitrobenzyl chloride and *iso*nitrosocamphor, 8.
$C_{17}H_{20}O_4N_2$ (m. p. 114°), from the interaction of *p*-nitrobenzyl bromide and *iso*nitrosocamphor, 9.
$C_{17}H_{20}O_4N_2$ (m. p. 175°), from the interaction of *p*-nitrobenzyl chloride and *iso*nitrosocamphor, 8.
$C_{18}H_{22}O_5$, from the expressed oil of nutmeg, 198.
$C_{18}H_{14}O_9N_4$, from β-naphthol and 2 : 3 : 5-trinitro-4-acetylaminophenol, 211.
$C_{23}H_{20}O_2$, from ethyl phenylpropiolate, acetophenone, and sodium ethoxide, 52.
$C_{27}H_{46}O_2$, and its acyl derivatives, from the oxidation of cholesterol 121.
$C_{31}H_{48}O_3$, from olive leaves, 117.
$C_{34}H_{50}O_5$, and its diacetate, from the oxidation of dicholesteryl ether, 121.
Succinic acid, alkaloidal salts, and their optical activity, 61.
Sucrose, conductivity and viscosity of solutions of, 187.
and lithium chloride, conductivity and viscosity of mixtures of solutions of, 187.
Sulphides, aromatic, interaction of with hydrogen dioxide, 216.

Sulphination of phenolic ethers and the influence of substituents, 61.
Sulphinic acids and sulphonic acids, aromatic, alkaloidal salts, and their rotatory power, 195.
Sulphoacetic acid, chloro-, strychnine salts and their optical activity, 99.
Sulphobenzylethyl*iso*butylsilicyl oxide, metallic, bornylamine, cinchonidine, cinchonidine hydrogen, and menthylamine salts, 224.
dl-Sulphobenzylethyl*iso*butylsilicyl oxide, resolution of, and the properties of the optically active acids, and their amine salts, 236.
dl-Sulphobenzylethylpropylsilicyl oxide, decomposition and resolution of, 47.
Sulphobenzylethylpropylsilicyl oxides, optically active, and their metallic, amine, and alkaloidal salts, 47.
Sulphobenzylethylsilicone and its salts, 25.
Sulphonic acids and sulphinic acids, aromatic, alkaloidal salts, and their rotatory power, 195.
Sulphoxides, preparation of, 216.
Sulphur, bi-, quadri-, and sexa-valent, influence of, on rotatory power, 195.
Thionyl chloride, action of, on the methylene ethers of catechol derivatives, 50, 60.
Sulphuric acid, viscosity of fuming, 270.
Trithionates of the alkali metals, 199.
Tetrathionates of the alkali metals, 199.
Syntheses with the aid of monochloromethyl ether, 212.
with phenol derivatives containing a mobile nitro-group, 197.

Tannic acid, action of reducing agents on, 272, 273.
estimation of, 273.
Tartaric acid, rotation of, in aromatic halogen derivatives, 125.
rotation of, in aromatic nitro-derivatives, 216.
Tautomerism, the enol-ketonic, 224.
Tellurium *di*cyanide and its compound with ether, 269.
Teloidine and its additive salts, 234.
Terpenes, contributions to the chemistry of the, 31.
experiments on the synthesis of, 64, 228.
Terpineols, *d*- and *l*-, synthesis of, 228.
Tetramethoxyanthraquinone, 52.
Tetramethoxy-2-benzoylbenzoic acid and hydroxy-, 52.
1 : 4 : 5 : 8-Tetramethylnaphthalene, absorption spectra of, 147.
Tetranaphthyl, absorption spectra of, 147.
Thallium, interaction of, with organic halogen compounds, 194.
quantitative separation of, from silver, 75.
Thallium ion, subvalent, existence of, in aqueous solutions, 76.
THERMOCHEMISTRY :—
Temperatures, high, and high pressures, apparatus for experiments at, 131.
Transition points, determination of, 213.
Transition temperatures, influence of foreign substances on, and the determination of molecular weights, 26.
Thetines, phenolic, and their reaction with benzoyl chloride, 123.
Thiocarbamide and ammonium thiocyanate, isomerism of, 135.
Thiocyanates containing an electronegative group, constitution of, 73.
Thionaphthen derivatives, synthesis of, from styrenes and thionyl chloride, 237.
Thionaphthen, *hexa*chloro- and 1:2-*di*chloro-4:5(or 5:6)-*di*hydroxy-, and its dibenzoyl derivative, 238.
Thionyldiglycollic acid and its salts, preparation of, 216.
Thoria, reduction of, by carbon, 188.
Thorianite, traces of a new tin-group element in, 60.
Thymol, 2-bromo-, bromonitro-, and 2-nitro-, 73.
Tin, the electroanalytical deposition of, 189.
Tin-group, new element of the, in thorianite, 60.
Tissues, distribution of phosphoproteins in, 200.
Titani-dihydroxymaleic acid, 133.
Titanium, detection of, 133.
Toluene, *o*-, *m*-, and *p*-chloro- and -nitro-, oxidation of, 195.
p-nitro-, action of caustic alkalis on derivatives of, 201.
ω-*iso*nitro-, velocity of transformation of, 135.
m-Toluic acid, 5-bromo-6-hydroxy-, 73.
p-Toluic acid, 2-hydroxy-, preparation and reduction of, 187.
p-Toluidides, anilides, and α-naphthalides of normal fatty acids, melting points of, 120.
Tolyl-5-arsonic acid, 2-amino-, and its sodium salt and its *N*-acetyl derivative, 143.

p-Tolylbenzylmethylallylammonium iodide and hydrogen tartrate, resolution of, 212.
Triazoacetaldehyde, 227.
Triazoacetic acid, dissociation constants of, 114.
1-Triazobutanone-2 and its semicarbazone and its oxime and its *p*-toluenesulphonyl derivative and 3-Triazobutanone-2 and its semicarbazone, 54.
Triazo-compounds, refraction and dispersion of, 114.
Triazoethyl alcohol (2-*triazoethanol*-1) and its acetate and *p*-nitrobenzoate, 227.
Triazo-group, the, 54, 102, 143, 226, 227.
α-Triazopropionic acid and its ethyl ester, silver salt, and amide, 54.
resolution of, and its reduction to alanine, and the lævo-acid and its brucine salt, ethyl ester, and amide, 226.
dissociation constants of, 114.
β-Triazopropionic acid, ethyl ester, 54.
Tribenzyl-silicol and -silicyl chloride, 25.
Trimethoxyanthraquinone, hydroxy-, 62.
Trimethoxy-2-benzoylbenzoic acid, 2′:3′:4′-(or 3′:4′:5′-), 52.
3:4:7-Trimethylcoumarin and its additive salts, oxime, and phenylhydrazone, 26.
Trimethyl*cyclo*hexenone (iso*phorone*), and some homologues, synthesis of, 281.
1:1:5-Trimethyl-Δ^4-*cyclo*hexenone-3 and its oxime and semicarbazone, 130.
Trimethylsulphine perbromides and periodides, 191.
3:4:7-Trimethylthiocoumarin, 26.
Triphenylethylsilicane, 12.
Triphenylmethane, absorption spectrum of, 33.
oxidation of, 195.
nature of the impurity found in preparations of, 94.
Triphenylmethane series, cause of colour in the, 206.
Triphenylmethylsilicane, 12.
Trixanthyl derivatives, new, 205.
Tropine and its derivatives, affinity values of, 280.
Tungsten oxide, reduction of, by carbon, 188.

Umbellulone, constitution of, 23.
Unsaturation and optical activity, relation between, 61, 186, 195.
Uranium *di*oxide, reduction of, by carbon, 188.
Uric acid derivatives, affinity constants of, as determined by the aid of methyl-orange, 50.

Valency, new theory of, 14, 122.
Vanillin, new isomeride of, from the root of a species of Chlorocodon, 62.
Vapour density, new method of determining, 8.
Viscosity and chemical constitution, relation between, 213, 224.
and conductivity of aqueous solutions, 187.
of solutions, 121.
determinations at high temperatures, 146.

Walden inversion, contribution to the chemistry of the, 91.
Water, conductivity, preparation of, 47.
chemical action of radium emanation on, 132, 133.
Weights, molecular, determination of, and the influence of foreign substances on transition temperatures, 26.
Werner's theory, criticism of, 14, 122.
Women, question of admitting, to the Fellowship of the Society, 203, 277.

Xanthyl derivatives, new, 204.
Xenon, density of, 272.
o-Xylene, nitro-derivatives of, 58.

Zinc mercuric cyanide, formula of, 135.
Zirconium, atomic heat and atomic volume of, 170.
Zirconium oxide (*zirconia*), reduction of by carbon, 188.

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Thursday, January 16th, 1908, at 8.30 p.m., Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

Messrs. F. Buckney, J. E. L. Moore, W. H. Nuttall, and D. Willott were formally admitted Fellows of the Society.

The PRESIDENT announced that the Council had recommended the following gentlemen as Honorary and Foreign Members to be balloted for at the next meeting of the Society: Messrs. J. A. Le Bel, H. L. Le Chatelier, A. E. J. Gautier, A. Haller, J. W. Hittorf, T. W. Richards, and O. Wallach.

Certificates were read for the first time in favour of Messrs.:

Robert Barton, jun., 48, Wellclose Mount, Leeds.
Harry James Brown, Pembrey Lead Works, Burry Port.
Hans Thacher Clarke, Gayton Corner, Harrow.
Arnold Merrick, 66, Rothbury Terrace, Newcastle-on-Tyne.
Arthur Stead, B.Sc., 113a, Kellner Street, Bloemfontein, O.R.C.
Thomas Marshall Tyson, 2, Osborne Road, Forest Gate, E.
David Thomas Williams, 9, Calvert Terrace, Swansea.
Francis Charles Benjamin Wood, Deurne, nr. Antwerp, Belgium.

A certificate was authorised by the Council under Bye-Law I (3) in favour of:

Joseph Valentine Francies, Engineering College, Sibpur, Calcutta.

The Council has ordered the following letter and report to be printed in the Journal and Proceedings of the Society:

GOVERNMENT LABORATORY,
CLEMENT'S INN PASSAGE,
STRAND, LONDON, W.C.
13*th November*, 1907.

GENTLEMEN,

I have the honour to forward you, for presentation to the Council of the Chemical Society, the Report of the International Committee on Atomic Weights, 1908, to which I have appended, as desired by them, the names of Professors Ostwald and Urbain.

It will be seen that since our last Report a number of important re-determinations of atomic weights have been published, and the existing table in consequence reveals a number of small inconsistencies due to the original data from which the values are derived. We think it is inopportune at present to attempt to recalculate these values as the work known to be in progress on certain fundamental constants, to which reference was made in our last Report, has not yet been published. We have good reason to believe, however, that it will soon make its appearance, and we hope to be able to present an amended table with our Report for next year.

I am, Gentlemen,
Your obedient Servant,
T. E. THORPE.

The Hon. Secretaries,
The Chemical Society,
Burlington House,
London, W.

Report of the International Committee on Atomic Weights, 1908.

Since the preparation of our report for 1907, several important determinations of atomic weights have been published. They are, briefly, as follows:

Nitrogen.—Richards and Forbes (*J. Amer. Chem. Soc.*, 1907, **29**, 808; *Zeitsch. anorg. Chem.*, 1907, **55**, 34) have re-determined the ratio between Ag and NO_3, as shown in the composition of silver nitrate. The ratio found, with all corrections applied, is $Ag : NO_3 = 100 : 57{\cdot}479$. Hence, if $Ag = 107{\cdot}930$, $N = 14{\cdot}037$, and if $N = 14{\cdot}008$, $Ag = 107{\cdot}880$. In short, the higher atomic weight hitherto assigned to silver is inconsistent with the lower value for nitrogen as found in several recent investigations.

Sulphur.—Richards and Jones (*J. Amer. Chem. Soc.*, 1907, **29**, 826 ; *Zeitsch. anorg. Chem.*, 1907, **55**, 72) have measured the ratio between Ag_2SO_4 and AgCl. From the data obtained, if Ag = 107·930, S = 32·113 ; a value much higher than that commonly accepted. If Ag = 107·880, then S = 32·069, which is near the figure given in our former tables. Additional evidence relative to this constant is much to be desired, for it influences the determination of many other atomic weights, especially those of the rare-earth metals.

Potassium.—From the ratios Ag : KCl and AgCl : KCl, Richards and Staehler (*J. Amer. Chem. Soc.*, 1907, **29**, 623 ; *Ber.*, 1906, **39**, 3611) find K = 39·114, when Ag = 107·930 and Cl = 35·473. From the corresponding bromide ratios, with Br = 79·953, Richards and Mueller (*J. Amer. Chem. Soc.*, 1907, **29**, 639 ; *Zeitsch. anorg. Chem.*, 1907, **53**, 423) find K = 39·1143 and 39·1135. The final result of both researches is K = 39·114, a distinct lowering of the constant in question.

Manganese.—Atomic weight re-determined by Baxter and Hines (*J. Amer. Chem. Soc.*, 1906, **28**, 1560 ; *Zeitsch. anorg. Chem.*, 1906, **51**, 202) from analyses of the chloride and bromide. The mean of their very concordant determinations is Mn = 54·957, when Ag = 107·930.

Cobalt.—From new analyses of the chloride, Baxter and Coffin (*J. Amer. Chem. Soc.*, 1906, **28**, 1580 ; *Zeitsch. anorg. Chem.*, 1906, **51**, 171) find Co = 58·997, or 59 in round numbers. This confirms the earlier determinations by Richards and Baxter.

Indium.—Mathers (*J. Amer. Chem. Soc.*, 1907, **29**, 485 ; *Ber.*, 1907, **40**, 1220), from analyses of indium chloride, found In = 114·88. From the bromide, In = 114·86. The author recommends the adoption of the rounded-off value, 114·9, when Ag = 107·93, Cl = 35·473, and Br = 79·953.

Tellurium.—Norris (*J. Amer. Chem. Soc.*, 1906, **28**, 1675), by twelve concordant reductions of the basic nitrate, $2TeO_2 \cdot HNO_3$ to TeO_2, found the atomic weight of tellurium to be 127·48, when N = 14·01. With N = 14·04, Te = 127·64, which is in better agreement with other recent determinations. The true cause of the difference is not clear.

Neodymium.—Holmberg (*Zeitsch. anorg. Chem.*, 1907, **53**, 83) has re-determined the atomic weight of this element by synthesis of the sulphate from the oxide. In mean, when S = 32·06, Nd = 144·08. This is higher by 0·48 than the value given in our table.

Dysprosium.—In two series of determinations, based upon the ignition to oxide of the octohydrated sulphate, Urbain and Demenitroux (*Compt. rend.*, 1906, **143**, 598) find for the atomic weight of dysprosium values ranging between 162·29 and 162·75. In mean, Dy = 162·53.

Radium.—In a new series of three determinations, made on about 4 decigrams of the carefully-purified chloride, Madame Curie (*Compt. rend.*, 1907, **145**, 422) has found Ra = 226·18, when Ag = 107·8 and Cl = 35·4. With Ag = 107·93 and Cl = 35·45, Ra = 226·45. This is more than a unit above her previous measurements.

From the data here given, and from those cited in previous reports, it is evident that the entire table of atomic weights is in need of revision. The values assigned to K and Na are too high; those given to Cl and S are too low, and these constants affect the determinations of many others. They depend, however, upon the atomic weight of silver, which is probably, but not certainly, as low as 107·88. It is well known that work upon these fundamental constants is now nearing completion in several laboratories, notably under T. W. Richards, W. A. Noyes, and probably other investigators also. Within a few months, it should be possible to enter upon a satisfactory revision of the table, a task which would be unsatisfactory if undertaken now. It is true, as Brauner has suggested, that the present table contains inconsistencies, but they are small in amount, and are due to inconsistencies in the original data from which the values are derived. In our next report, we hope to recompute the entire table; but meanwhile, awaiting the completion of the researches which we know to be in progress, we prefer to leave the table practically unchanged. A conservative policy seems to be safer than one of haste, and the delay of another year will do no harm. One exception to the rule may, however, be made. Dysprosium, with the atomic weight 162·5, may now be properly added to the list of the chemical elements, and we recommend its insertion in the table.

It is with the deepest regret that we record the loss, by death, in February last, of our distinguished colleague, Prof. Moissan. The Chemical Society of Paris has designated Monsieur G. Urbain as his successor upon this Committee.

(Signed) F. W. Clarke,
W. Ostwald,
T. E. Thorpe,
G. Urbain.

International Atomic Weights.

		O=16.			O=16.
Aluminium	Al	27·1	Molybdenum	Mo	96·0
Antimony	Sb	120·2	Neodymium	Nd	143·6
Argon	A	39·9	Neon	Ne	20
Arsenic	As	75·0	Nickel	Ni	58·7
Barium	Ba	137·4	Nitrogen	N	14·01
Bismuth	Bi	208·0	Osmium	Os	191
Boron	B	11·0	Oxygen	O	16·00
Bromine	Br	79·96	Palladium	Pd	106·5
Cadmium	Cd	112·4	Phosphorus	P	31·0
Cæsium	Cs	132·9	Platinum	Pt	194·8
Calcium	Ca	40·1	Potassium	K	39·15
Carbon	C	12·00	Praseodymium	Pr	140·5
Cerium	Ce	140·25	Radium	Rd	225
Chlorine	Cl	35·45	Rhodium	Rh	103·0
Chromium	Cr	52·1	Rubidium	Rb	85·5
Cobalt	Co	59·0	Ruthenium	Ru	101·7
Columbium	Cb	94	Samarium	Sa	150·3
Copper	Cu	63·6	Scandium	Sc	44·1
Dysprosium	Dy	162·5	Selenium	Se	79·2
Erbium	Er	166	Silicon	Si	28·4
Europium	Eu	152	Silver	Ag	107·93
Fluorine	F	19·0	Sodium	Na	23·05
Gadolinium	Gd	156	Strontium	Sr	87·6
Gallium	Ga	70	Sulphur	S	32·06
Germanium	Ge	72·5	Tantalum	Ta	181
Glucinum	Gl	9·1	Tellurium	Te	127·6
Gold	Au	197·2	Terbium	Tb	159·2
Helium	He	4·0	Thallium	Tl	204·1
Hydrogen	H	1·008	Thorium	Th	232·5
Indium	In	115	Thulium	Tm	171
Iodine	I	126·97	Tin	Sn	119·0
Iridium	Ir	193·0	Titanium	Ti	48·1
Iron	Fe	55·9	Tungsten	W	184
Krypton	Kr	81·8	Uranium	U	238·5
Lanthanum	La	138·9	Vanadium	V	51·2
Lead	Pb	206·9	Xenon	Xe	128
Lithium	Li	7·03	Ytterbium	Yb	173·0
Magnesium	Mg	24·36	Yttrium	Yt	89·0
Manganese	Mn	55·0	Zinc	Zn	65·4
Mercury	Hg	200·0	Zirconium	Zr	90·6

Of the following papers, those marked * were read :—

***1. "Colour and constitution of azo-compounds. Part II. The salts of *p*-hydroxyazo-compounds with mineral acids." By John Jacob Fox and John Theodore Hewitt.**

In several communications of one of the present authors, the view has been advanced that, whilst *p*-hydroxyazobenzene has a constitution which is correctly expressed by its name, the salts which it forms with mineral acids are derived from the tautomeric quinonehydrazone. W. B. Tuck (*Trans.*, 1907, **91**, 449), from a consideration of the absorption spectra of benzeneazophenol and its ethyl ether in alcoholic and concentrated hydrochloric acid solutions, concludes that the hydrochlorides of both compounds "have similar structures, and consequently the hydrochlorides of the free hydroxyl substances have an azo-structure."

From an examination of benzeneazo-α-naphthol and its ethyl ether, the present authors agree with Tuck's statement as to similarity of structure, but deny that this structure is of azo-type, as the reactions of hydroxyazo-compounds in concentrated acid solution negative this view.

F. Baker's attempt (*Trans.*, 1907, **91**, 1490) to formulate these compounds as carbonium salts is unsatisfactory ; it requires quinquevalent nitrogen in a hitherto unobserved form, whilst the dihydrochloride of dimethylaminobenzene-azo-α-naphthol (prepared by the authors) would have to be written :

The most conclusive evidence is given by the fact that the hydrochloride of *p*-bromobenzeneazophenol and the hydrobromide of *p*-chlorobenzeneazophenol, which, according to Baker, should both have the constitution :

are actually different substances, yielding the components from which they are respectively derived when decomposed by alkali.

The present authors suggest, instead of the formulæ hitherto proposed, the constitution of oxonium salts for these compounds, for example :

$$C_6H_5\cdot NH\cdot N{:}C_6H_4{:}O(H \text{ or } C_2H_5)Cl.$$

The formulation of the salts of the ethers and parent substances is thus the same, whilst the reactions in concentrated sulphuric acid solution are easily explained.

Discussion.

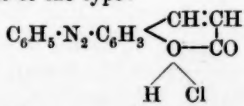
Mr. Tuck said that the absorption spectra of the hydrochlorides of the free *p*-hydroxyazo-compounds and their ethers were the same, and this fact showed that their constitutions therefore were identical. If this was so, then Dr. Hewitt's conclusion (*Ber.*, 1897, **30**, 1625) that hydrochloric acid converted the *p*-hydroxyazo-compounds into quinonehydrazones must be incorrect. This was now accepted by Dr. Hewitt.

As the absorption spectra of these hydrochlorides agreed with that of azobenzene hydrochloride, one must conclude that the acid was combined in precisely the same manner in each case, that is, the hydrochlorides were true azo-derivatives.

The objection to Dr. Hewitt's formula for the hydrochlorides lay in the fact that it was impossible to assign the same structure to azobenzene hydrochloride as he did to hydroxyazo-hydrochlorides.

Mr. Baly pointed out that Dr. Hewitt's explanation seemed to fail in two respects. In the first place, it could not account for the formation of the deeply-coloured hydrochloride of azobenzene where, of course, the oxonium structure was excluded. Moreover, the change of colour on adding hydrochloric acid to a neutral solution of azobenzene was precisely of the same character as Dr. Hewitt had shown in the case of the hydroxyazo-compounds. In the second place, the addition of the acid molecule to the oxygen atom with the formation of the oxonium salt would undoubtedly decrease the colour of the compound in the sense that the absorption band would shift towards the *blue*. In the hydrochlorides of the hydroxyazo-compounds, the absorption band had shifted towards the *red*, causing the salt to be bluer than the parent substance. This decrease in colour would be caused by the decrease in the residual affinity of the system, due to the oxygen becoming quadrivalent.

Mr. H. V. Mitchell drew attention to the fact that he had been unable to prepare a hydrochloride of benzeneazocoumarin (*Trans.*, 1905, **87**, 1231), whereas if the view put forward by the authors were correct, a hydrochloride of the type:



might have been expected.

Dr. Hewitt, in reply, pointed out that Mr. Tuck stated definitely in his paper "the hydrochlorides of the free hydroxyl substances have an azo-structure," whilst Mr. Baly's arguments derived from the properties of benzeneazo-*p*-cresol and its derivatives depended for their validity on this substance being a quinonehydrazone. Since this point was still disputed and the bulk of the evidence seemed to be in favour of a hydroxylic structure for the free *o*-azo-compounds, the arguments lost in weight.

No surprise need be occasioned by Mr. Mitchell's inability to obtain a hydrochloride from benzeneazocoumarin, for the lactonic oxygen atom would scarcely have pronounced basic properties, whilst Professor Armstrong's arguments against the formula depended on supposed basicity of the benzene nucleus and non-existence of oxonium salts. Basicity of the benzene nucleus scarcely accorded with the feeble acidity of phenol and the diminishing basicity observed in amines by introduction of benzene nuclei, whilst the possibility of oxonium salt formation was recognised by all who had made a comparative study of the xanthhydrol and acridinium groups.

***2. "A new method of determining vapour densities. Part I." By Philip Blackman.**

***3. "Studies in the camphane series. Part XXV. Action of diazomethane on the two modifications of *iso*nitrosocamphor." By Martin Onslow Forster and Henry Holmes.**

When diazomethane acts on the stable *iso*nitrosocamphor (m. p. 152°) dissolved in ether, the *N*-methyl ether is produced, whilst the unstable modification (m. p. 114°), treated with a deficit from one molecular proportion of the agent, merely undergoes isomeric change to the less fusible variety; in view of this observation, some caution will be necessary in drawing conclusions regarding the structure of a compound based on its behaviour towards diazomethane. The benzaldoximes do not behave in the same way, ben*zanti*-aldoxime (m. p. 35°) yielding the *O*-methyl ether, whilst the *syn*-aldoxime (m. p. 128°) remains unchanged.

By the action of *p*-nitrobenzyl chloride on an alcoholic solution of *iso*nitrosocamphor in presence of sodium ethoxide, three products arise. The *compound*, $C_{17}H_{20}O_4N_2$, having the composition of a nitrobenzyl ether of *iso*nitrosocamphor, crystallising in pale brown prisms, melting at 175°, and having $[\alpha]_D$ 123·0°; the *compound*, $C_{17}H_{18}O_3N_2$, forming lustrous, transparent, yellow plates, melting at 214°, with

$[\alpha]_D$ −65·3°, and an *oil*, which is characterised by developing an intense blue coloration when caustic alkali is added to a solution in methyl, ethyl, or *iso*butyl alcohol. If silver oxide is substituted for sodium ethoxide as a condensing agent, and *p*-nitrobenzyl chloride is replaced by the bromide, an isomeric *compound*, $C_{17}H_{20}O_4N_2$, is produced, crystallising in colourless prisms, melting at 114°, and having $[\alpha]_D$ 138·0°.

On mixing an ethereal solution of iminocamphor with formaldehyde, no change occurs until a trace of acid is added, when the product, dissolved in alcohol, develops an intense, magenta-red coloration with caustic alkali; ether precipitates from this solution an unstable solid, having the appearance of indigo, and yielding camphorquinone, formaldehyde, and ammonia with dilute sulphuric acid.

Camphorquinone is rapidly oxidised by an aqueous solution of hydrogen peroxide to camphoric anhydride.

The *N-ethyl* ether of *iso*nitrosocamphor, $C_8H_{14}<\begin{matrix}C:NEt:O\\CO\end{matrix}$, produced in association with the *O*-ethyl ether when ethyl iodide acts on *iso*nitrosocamphor in presence of sodium ethoxide, melts at 57°, and has $[\alpha]_D$ 248·1°; it is readily hydrolysed by acids, yielding camphorquinone and ethylhydroxylamine.

Discussion.

Mr. Baly said that the formulæ for the two forms of *iso*nitrosocamphor which Dr. Forster referred to as being given by Baly, Marsden, and Stewart had resulted from the adverse criticism their paper received when it was read. When their paper was first written, they had inclined to the nitroso-formula, and it was therefore extremely interesting to find that Dr. Forster's experiments seemed to support this view. As regards the new formula which Dr. Forster had given to the *N*-ethers of *iso*nitrosocamphor, he (Mr. Baly) spoke strongly in favour of it from the point of view of the absorption spectra of these substances. They exhibited a very marked absorption band, exactly the same as that which might be described as the middle band of *p*-benzoquinone. The latter substance in aqueous solution exhibited three absorption bands, the middle one of which was absent from the spectrum of an alcoholic solution. It had occurred to him that the middle band might be explained by the formation of a hydrate of quinone, and so the absorption spectrum was examined of an alcoholic solution of *p*-benzoquinone to which a little alcoholic solution of hydrogen chloride had been added. The absorption spectrum then showed only the middle band, and was, indeed, the same as that of the *N*-ethyl ethers of *iso*nitrosocamphor. Seeing that exactly the same was observed with camphorquinone, it did not seem unreasonable that

the hydrogen chloride molecule combined by virtue of the quadri valency of one of the oxygen atoms, and that in the case of camphorquinone a compound was formed of the type: $C_8H_{14}<\begin{matrix}C{:}O{:}HCl\\ |\\ C{:}O\end{matrix}$. The analogy between this and Dr. Forster's new formula was sufficient to account for the similarity in the spectra of camphorquinone dissolved in alcohol containing some hydrogen chloride and the *N*-alkyl ethers of *iso*nitrosocamphor. There was no doubt that the absorption spectra offered striking evidence against either of the varieties of *iso*nitrosocamphor having the formula $C_8H_{14}<\begin{matrix}C{:}NH{:}O\\ |\\ C{:}O\end{matrix}$, for there was no resemblance between the spectra of the *iso*nitroso-compounds and the *N*-alkyl ethers.

Dr. Hewitt asked Mr. Baly if he had convinced himself that the colourless additive product of benzoquinone and hydrochloric acid was not really chloroquinol.

4. "The oxidation of aromatic hydrazines by metallic oxides, permanganates, and chromates." By Frederick Daniel Chattaway.

Primary aromatic hydrazines are readily attacked by most substances capable of giving up oxygen at all easily. The products are in the main the same as those which are formed by free oxygen.

The chief action, which results in the replacement of the hydrazino-group by hydrogen and the liberation of nitrogen, is generally accompanied by secondary ones which take place to a relatively very small extent. By these secondary actions, hydrocarbons of the diphenyl group or azo-derivatives are formed. Diazo-compounds are only obtained in presence of acids; in presence of alkalis, they are not formed.

Potassium chromate oxidises primary aromatic hydrazines very easily, and gives a theoretical yield of nitrogen and hydrocarbon. This reaction affords the most convenient method yet described for replacing an aromatic amino-group by hydrogen, the diazonium group yielded by it being first reduced to the hydrazino-group and this then replaced by hydrogen through oxidation with potassium chromate.

All the evidence obtained shows that the explanation of the behaviour of primary aromatic hydrazines on oxidation recently put forward by the author is correct (*Trans.*, 1907, **91**, 1324), namely, that an unstable hydroxyhydrazine is first produced, which, in presence of caustic alkali, immediately breaks down into hydrocarbon, nitrogen, and water:

$$\begin{matrix}R{\cdot}N{\cdot}H\\ |\\ H{\cdot}N{\cdot}OH\end{matrix} \longrightarrow \begin{matrix}R\\ |\\ H\end{matrix} + \begin{matrix}N\\ \|\\ N\end{matrix} + \begin{matrix}H\\ |\\ OH\end{matrix}.$$

Copper oxide easily gives up its oxygen to phenylhydrazine, and if the reduction is conducted under suitable conditions the metal can be deposited on glass in the form of a fine mirror. The film of metal thus laid down is as brilliant as a similar deposit of silver, and shows the beautiful red colour of polished copper.

5. "**Studies in fermentation. Part II. The mechanism of alcoholic fermentation.**" **By Arthur Slator.**

The velocity of the conversion of dextrose, lævulose, galactose, and mannose into alcohol and carbon dioxide by the action of living yeast has been measured in the manner already described (*Trans.*, 1906, **89**, 128). The main results are as follows :

1. The rate of fermentation of dextrose, lævulose, galactose, and mannose is approximately independent of the concentration of the sugar between the concentrations 1 gram to 10 grams per 100 c.c.

2. The fermentation of dextrose and lævulose under all conditions proceeds with approximately equal velocities.

3. The temperature-coefficient is almost the same in the case of the fermentation of dextrose, lævulose, and mannose, but is somewhat less in the case of the fermentation of galactose.

4. Many yeasts (very probably all yeasts) are unable to ferment galactose unless the yeast has been grown in the presence of this sugar.

5. The ratio of the rate of fermentation of dextrose to mannose varies greatly, depending on the treatment the yeast has undergone.

6. When two sugars are fermented simultaneously in the same solution, interference takes place between the reactions.

7. The velocity of fermentation by living yeast can be easily lessened by the addition of certain inhibiting agents, but cannot be appreciably raised.

8. In all probability the fermentation of sugars by preparation from yeast proceeds on the same lines as that by living yeast, but the reaction is much complicated by secondary changes.

The supposition that the reaction which has the main control of the velocity of fermentation is the decomposition of a stable compound between the enzyme and the sugar can be made to explain these results. Possibly three enzymes are present in yeast which will ferment the four sugars : glucozymase which ferments dextrose and lævulose, galactozymase which ferments galactose, and mannozymase which ferments mannose.

6. "Organic derivatives of silicon. Part IV. The sulphonation of benzylethylpropylsilicyl oxide and of benzylethyldipropylsilicane." By Herbert Marsden and Frederic Stanley Kipping.

Although the optically-active silicon compounds described recently (Kipping, *Trans.*, 1907, **91**, 212) were actually prepared from the product of the sulphonation of benzylethylpropylsilicol, their investigation indicated that they were sulphonic derivatives of benzylethylpropylsilicyl oxide. As this view of their constitution seemed to need some confirmation, the authors have prepared benzylethylpropylsilicyl oxide itself and sulphonated it with sulphuric and with chlorosulphonic acid; in both cases there was formed an acid having the composition of a derivative of the oxide and identical with the compound which has been resolved; any uncertainty regarding the composition of the optically-active compounds is thus removed.

The sulphonation of phenylbenzylethylpropylsilicane with chlorosulphonic acid gave results similar to those obtained with sulphuric acid, that is to say, the phenyl group was eliminated and the product was a sulphonic derivative of benzylethylpropylsilicyl oxide identical with that previously described.

Benzylethyldipropylsilicane, $BzEtPr_2Si$, has been prepared and converted into *benzylethyldipropylsilicanesulphonic acid*,

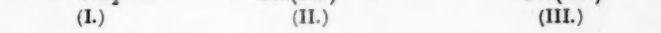
$$EtPr_2Si\cdot CH_2\cdot C_6H_4\cdot SO_3H,$$

with the aid of chlorosulphonic acid; the *l-menthylamine*, *cinchonidine*, and *quinine* salts of this acid resemble very closely the corresponding salts of *dl*-benzylmethylethylpropylsilicanesulphonic acid (*loc. cit.*, p. 717), a fact which indicates that the latter are mere mixtures of their optically-isomeric components.

Diphenylethylsilicyl chloride, $Ph_2EtSiCl$, a colourless liquid boiling at 206—208° (50 mm.), *diphenylethylsilicyl oxide*, $(Ph_2EtSi)_2O$ (m. p. 65·5°), *triphenylethylsilicane*, Ph_3EtSi (m. p. 76°), and *triphenylmethylsilicane*, Ph_3MeSi (m. p. 67—67·5°), were also described.

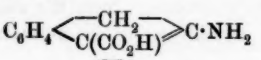
7. "The formation and reactions of imino-compounds. Part VI. The formation of derivatives of hydrindene from *o*-phenylenediacetonitrile." By Charles Watson Moore and Jocelyn Field Thorpe.

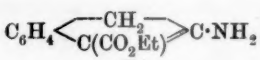
When *o*-phenylenediacetonitrile (I) is warmed in alcoholic solution containing a trace of sodium ethoxide, it is completely converted into *α-cyano-β-iminohydrindene* (II), which can be hydrolysed to *α-cyano-β-hydrindone* (III):

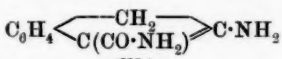


(I.) (II.) (III.)

α-Cyano-β-iminohydrindene (II) is a neutral imino-compound, which is hydrolysed by dilute acids and does not evolve nitrogen with nitrous acid. If, however, the nitrile group is replaced by carboxyl, carboethoxyl, or the carboxylamino-group, the compounds formed are true bases. Thus *2-aminoindene-3-carboxylic acid* (IV), *ethyl 2-aminoindene-3-carboxylate* (V), and *2-aminoindenecarboxyl amide* (VI):

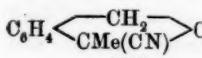

(IV.)

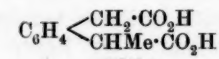

(V.)

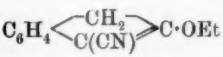

(VI.)

are all bases, which are not hydrolysed by dilute acids and evolve free nitrogen when treated with nitrous acid. There is no evidence that these compounds are capable of reacting in the imino-form.

α-Cyano-β-hydrindone (III) gives a well-defined *phenylhydrazone*, and on methylation yields *α-cyano-α-methyl-β-hydrindone* (VII), which gives *phenyleneaceticpropionic acid* (VIII) on hydrolysis. When, however, the ketone is treated with sodium ethoxide and ethyl iodide, the *O*-ethyl derivative, *3-cyano-2-ethoxyindene* (IX), is alone produced:


(VII.)

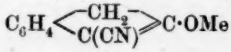

(VIII.)

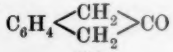

(IX.)

α-Cyano-β-hydrindone (III) reacts also as a phenol, since it can be readily alkylated by alkyl sulphates, yielding, with methyl sulphate, *3-cyano-2-methoxyindene* (X) and with ethyl alcohol and sulphuric acid, 3-cyano-2-ethoxyindene (IX) identical with the compound prepared by the alkylation of the ketone with sodium ethoxide and ethyl iodide. The constitution of these salts is shown by their hydrolysis with dilute acids to α-cyano-β-ketohydrindene.

It is therefore probable that groups greater than Me and CN cannot attach themselves to the α-carbon atom of β-hydrindone or β-iminohydrindene, and it is suggested that the term "stearic inhibition" should be applied to this phenomenon rather than "stearic hindrance."

β-Hydrindone (XI) can be prepared by distilling with steam a solution of 2-aminoindene-3-carboxylic acid (IV) in dilute sulphuric acid:


(X.)


(XI.)

This substance is quite stable when pure, and does not show any tendency to pass into a brown resin as stated in the literature.

8. "Valency." By John Albert Newton Friend.

The author suggested a new theory of valency by means of which many reactions receive explanations not forthcoming from the usually accepted theory. The theory was also considered in its relation to that of Werner.

9. "The esterification constants of the normal fatty acids." By John Joseph Sudborough and James Mylam Gittins.

The esterification constants of some sixteen of the more common normal fatty acids, from formic to stearic acid, have been determined. The value $E^{15°}_{MeOH}$ for formic is 1124; acetic, 104; propionic, 92; and from butyric to stearic acid the value remains nearly constant, varying from about 50 to 54.

10. "The anomalous behaviour of the hydrogen electrode in solutions of lead salts and the existence of univalent lead ions in aqueous solutions." By Henry George Denham and Arthur John Allmand.

An attempt has been made to measure the hydrolysis of lead salts by the hydrogen electrode, but results were obtained which were far higher than those recorded by Ley (*Zeitsch. physikal. Chem.*, 1899, **30**, 193), and it was also noticed that many hours were required for the electrode to give a constant potential. This has been proved to be due to the reaction :

$$Pb^{\cdot\cdot} + H \longrightarrow Pb^{\cdot} + H^{\cdot}$$

occurring at the platinum electrode.

The existence of plumbous acetate in aqueous solutions has been conclusively proved by carrying out an experiment of the type described by Richards, Collins, and Heimrod (*Zeitsch. physikal. Chem.*, 1900, **32**, 321) for copper and by Bose (*Zeitsch. Elektrochem.*, 1907, **13**, 477) for silver. In hot solution, lead reduces lead acetate to plumbous acetate, but the reaction is reversed in the cold, crystalline lead being deposited in the cold parts of the apparatus. The ionic reaction is evidently :

$$Pb^{\cdot\cdot} + Pb \longrightarrow 2Pb^{\cdot}.$$

It has also been proved that a rod of lead, immersed in a molar-normal solution of lead acetate, the upper part of which is kept hot by a steam-jacket, forms a thermo-electric cell. A weak thermo-current flows from the hot solution to the colder below, and, after a week, definite traces of spongy lead may be recognised at the junction of the hot and cold solutions.

11. "Amphoteric metallic hydroxides. Part I." By John Kerfoot Wood.

The author has investigated the amphoteric character of the hydroxides of arsenic and aluminium. Arsenic hydroxide is a very feeble base, the basic constant being of the dimensions of 1×10^{-14}. The acidic constant, as found by the saponification method, has a value of $6{\cdot}3 \times 10^{-10}$, and an $N/10$ solution of sodium metarsenite is hydrolysed to the extent of 1·4 per cent. at 25°. The dissociation constant of arsenious acid, as found by the conductivity method, has a value of $26{\cdot}5 \times 10^{-10}$.

Aluminium hydroxide is a weak base. The chloride is hydrolysed to the extent of about 4 per cent. at 25°, and is probably transformed into a basic chloride having the formula $Al(OH)Cl_2$. Sodium meta-aluminate in $N/10$ solution is hydrolysed to the extent of about 35 per cent. at 25°, the acidic constant of aluminium hydroxide being $6{\cdot}3 \times 10^{-13}$.

12. "The use of pyridine bases as halogen carriers." By William Ernest Cross and Julius Berend Cohen.

The authors have shown that the process of halogen substitution in the case of aceto-*p*-toluidide and other amides is preceded by the formation of additive compounds (*Proc.*, 1907, 23, 326), but attempts to effect substitution in a similar manner by means of the additive compounds of the pyridine bases with bromine failed.

The result, however, suggested the possibility of employing these bases as halogen carriers, an anticipation which has been confirmed by the following experiments.

Chlorobenzene.—Chlorine was passed into 50 grams of benzene containing a few drops of pyridine, and the mixture was warmed to 50°. The action proceeded rapidly with evolution of hydrogen chloride. The product was shaken with alkali, dehydrated, and distilled. Some unchanged benzene and a little dichlorobenzene were separated. The yield of pure chlorobenzene was 30 grams.

Chlorotoluenes.—The chlorination proceeds at the ordinary tempera-

ture. From 43 grams of toluene, 25 grams of mixed chlorotoluenes were obtained, b. p. 150—165°, together with a few grams of higher boiling products.

Bromobenzene.—A few drops of pyridine were added to a mixture of 50 grams of benzene and 120 grams of bromine, which were warmed to 25° in the water-bath. The action proceeds vigorously with the evolution of hydrogen bromide. The temperature was finally raised to 65—70°. The crude product, which boiled at 148—158°, amounted to 60 grams. The same result was produced with quinoline and *iso*-quinoline.

Dibromobenzene.—The *p*-dibromo-compound was obtained in a similar manner. From 33 grams of bromobenzene, 20 grams of the para-compound, m. p. 87°, were obtained, the remainder being unchanged bromobenzene. No ortho-compound was detected.

Bromotoluene.—Fifty grams of toluene yielded 87 grams of bromotoluene, b. p. 178—182°.

4-*Chloro*-1-*bromotoluene.*—Fifty-five grams of *p*-chlorotoluene gave 56 grams of chlorobromotoluene, b. p. 220—235°, and a small quantity of lower and higher boiling products.

α-*Bromonaphthalene.*—The α-compound was prepared by dissolving 25 grams of naphthalene in 100 c.c. of chloroform and adding 36 grams of bromine and a few drops of pyridine. The mixture was left in the cold for twenty-four hours. After purification, 35 grams of α-bromonaphthalene were obtained, b. p. 276—278°.

13. "Decomposition of hyponitrous acid." By Edward Divers.

By suddenly drenching dry silver hyponitrite or mercurous hyponitrite at a temperature but little below 30° with a mineral acid, not greatly diluted in the case of hydrochloric acid or sulphuric acid, and only sufficiently so in the case of nitric acid to avoid inducing its oxidising action, Rây and Gañguli * have obtained nitric acid and nitrogen as products of decomposition, in place of much of the nitrous oxide which was to be expected. This interesting observation throws much light on the nature of the decomposition of silver and mercury hyponitrites by heat. These authors, indeed, suggest that the presence of mineral acids has a "specific directive influence" in determining the form of the decomposition, but that is a notion without evident support. That sulphuric acid should be less effective in bringing about the decomposition is sufficiently accounted for by the fact that the comparative insolubility of silver and mercurous sulphates greatly impedes the action of this acid on the hyponitrites and the rise of temperature which attends it.

Through Rây and Gañguli's observations, we are at length in

* *Trans.*, 1907, **91**, 1866.

possession of much knowledge of what the products are when hyponitrous acid decomposes, without explosion, by the heat generated in liberating it from its salts. Since hyponitrous acid yields only nitric acid and nitrogen (water and nitrous oxide being here negligible), whilst silver hyponitrite or mercurous hyponitrite yields, besides these, much nitric oxide and some nitrous acid or nitric peroxide, we can now see that production of the latter substances is due to the unstable oxidised silver or mercury. Writing hyponitrous acid as H_2O,N_2O, and its silver salt as Ag_2O,N_2O, we see that $5N_2O$ become $4N_2+N_2O_5$, the water remaining unchanged in the former case, whereas the silver oxide in the latter case is reduced to metal, whilst its oxygen becomes active. Hence we obtain the two equations :

$$5H_2O_2N_2=4H_2O+4N_2+2HNO_3,$$

and

$$3Ag_2O_2N_2=4Ag+2N_2+2AgNO_3.$$

Similarly, the production of nitric oxide and peroxide is referable to the reducibility of oxidised silver or mercury, and could only come from hyponitrous acid through a highly improbable cumulative resolution of nitrous oxide.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Haskins, *H. D.*, and **Macleod**, *J. J. R.* Organic chemistry. Including certain portions of physical chemistry for medical, pharmaceutical, and biological students. pp. xi+367. ill. New York 1907. (*Recd.* 31/12/7.)

From the Publishers : Messrs. John Wiley and Sons.

Valentin, *William George.* Practical chemistry. 10th edition, by *W. R.* **Hodgkinson.** pp. xix+476. ill. London 1908. (*Recd.* 30/12/7.) From Professor W. R. Hodgkinson.

II. *By Purchase.*

Baumert, *Georg*, **Dennstedt**, *M.*, and **Voigtländer**, *F.* Lehrbuch der gerichtlichen Chemie. Band I. Der Nachweis von Giften und gesundheitsschädlichen Stoffen in Leichenteilen, Harn, Nahrungs-

und Genussmitteln, Gebrauchsgegenständen, Wasser, Luft und Boden. pp. xvi + 490. ill. Braunschweig 1907. (*Recd.* 18/12/07.)

Bersch, *Josef.* The manufacture of mineral and lake pigments. Containing directions for the manufacture of all artificial artists' and painters' colours, enamel colours, soot, and metallic pigments. Translated from the second revised edition by *Arthur C.* **Wright.** pp. xv + 476. London 1901. (*Recd.* 20/12/07.)

Bertelsmann, *W.* Die Entwicklung der Leuchtgaserzeugung seit 1890. (Sammlung, Vol. XII.) Stuttgart 1907. (*Recd.* 5/12/07.)

Hurst, *George H.* Painters' colours, oils, and varnishes: a practical manual. 4th edition. pp. viii + 519. ill. London 1906. (*Recd.* 20/12/07.)

Jost, *Ludwig.* Lectures on plant physiology. Authorised English translation by *R. J. Harvey* **Gibson.** pp. xiv + 564. ill. Oxford 1907. (*Recd.* 20/12/07.)

Journal of Agricultural Science. Edited by *R. H.* **Biffen,** *A. D.* **Hall,** *T. H.* **Middleton,** and *T. B.* **Wood.** Vol. I., &c. Cambridge 1905 +. (*Reference.*)

Müller, *Arthur.* Allgemeine Chemie der Kolloide. pp. x + 204. Leipzig 1907. (*Recd.* 18/12/07.)

Peters, *Edward Dyer.* The principles of copper smelting. pp. ix + 612. ill. New York 1907. (*Recd.* 20/12/07.)

Starling, *Ernest H.* Mercers' Company Lectures on recent advances in the physiology of digestion. Delivered in the Michaelmas Term, 1905, in the Physiological Department of University College, London. pp. x + 156. ill. London 1906. (*Recd.* 20/12/07.)

III. *Pamphlets.*

Arnott, *M. H.* The construction of drain gauges at Pusa. (From the *Mem. Dept. Agric. India,* **1,** 1907.)

Schüller, *Bernhard.* Carl Friedrich Mohr. (Reprint from the *Festschrift des Real-Gymnasiums zur Einweihungsfeier des Neubaues,* 1907.)

Singh, *Puran.* Researches on cantharidine, its extraction and determination. pp. 16. Lahore 1907.

LOTHAR MEYER MEMORIAL.

The Council has decided to make a donation of £10 to the Lothar Meyer Memorial Fund.

Many old pupils and admirers of the author of "Die Modernen Theorien der Chemie" may be desirous of contributing to this Memorial, and the Treasurer will be glad to receive, at an early date, subscriptions from Fellows and others to the Fund.

Cheques, &c., should be made payable to Dr. Alexander Scott, crossed "Lothar Meyer Memorial Fund A/c.," and sent to the Treasurer, Chemical Society, Burlington House, W.

ERRATUM.

1907. p. 305, line 5 from top, *for* "**alkalis**" *read* "alkali metals."

At the next Ordinary Meeting on **Thursday**, February 6th, 1908, at **8.30** p.m., there will be a ballot for the election of Honorary and Foreign Members and the following papers will be communicated:

"The metallic picrates." By O. Silberrad and H. A. Phillips.

"Organic derivatives of silicon. Part V. Benzylethylsilicane, dibenzylsilicane, and other benzyl- and benzylethyl-derivatives of silicane." By R. Robinson and F. S. Kipping.

"Some physico-chemical properties of mixtures of pyridine and water." By H. Hartley, N. G. Thomas, and M. P. Appleby.

"The constitution of umbellulone. Part III." By F. Tutin.

"The residual affinity of the coumarins and thiocoumarins as shown by their additive compounds." By A. Clayton.

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Issued 14/2/08

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 24. **No. 336.**

Thursday, February 6th, 1908, at 8.30 p.m., Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society owing to the death of Mr. W. A. Shenstone, F.R.S. (elected in 1876), and of Mr. R. J. Friswell (elected in 1871).

Certificates were read for the first time in favour of Messrs.:

Arthur John Allmand, B.Sc., Central Laboratories, Widnes.
William Henry Benson Baker, B.A., Frognal Dene, Hampstead, N.W.
Josiah Leonard Bowen, 8, West Field, Lightcliffe, near Halifax.
Charles Gilling, 30, Carnarvon Road, Barnet.
Alwyne Harcourt Meade, Cedar House, St. Neots.
Herbert Richard Neech, 20, Colegrave Street, Lincoln.
Thomas Richards Phillips, Stanhope House, Abergavenny.
Francis Edward Richards, B.Sc., County Secondary School, Redruth.
William Wheatley, B.A., 21, Bairstow Street, Preston.

A Ballot for the election of Honorary and Foreign Members was held, and the following were subsequently declared duly elected:

Armand Emile Justin Gautier.
Albin Haller.
Johann Wilhelm Hittorf.
Joseph Achille Le Bel.
Henry Louis Le Chatelier.
Theodore William Richards.
Otto Wallach.

Of the following papers, those marked * were read :—

***14. "The metallic picrates." By Oswald Silberrad and Henry Ablett Phillips.**

Older investigations on the picrates show so many discrepancies that a systematic revision of the work has been undertaken, with the result that the water of crystallisation and properties of the commoner salts have been definitely established. Several new salts were also described.

***15. "Some physico-chemical properties of mixtures of pyridine and water." By Harold Hartley, Noel Garrod Thomas, and Malcolm Percival Applebey.**

With the view of examining the effect of the gradual replacement of water by pyridine on the electrical conductivity of salt solutions, and of tracing a connexion between the properties of the solvent and of the solution, the following physical constants have been determined : the density, viscosity, and surface tension of pyridine-water mixtures at 0° and 25°, the density and viscosity of one-eighth weight-normal solutions of lithium nitrate in a series of mixtures at 0° and 25°, and the molecular conductivity of these solutions at various dilutions at the same temperatures.

The density and viscosity curves all show a maximum deviation from the line joining the end values in the neighbourhood of 30 mol. per cent. pyridine, both at 0° and 25°. No evidence was found for the existence of the discontinuities described by Dunstan, Thole, and Hunt (*Trans.*, 1907, **91**, 1718), all the observations lying on smooth curves.

By the application of Stokes' equation respecting the limiting velocity of a small sphere moving in a viscous medium under the influence of a constant force, the variation in the size of the solvent atmospheres attached to the ions at infinite dilution has been calculated.

It was shown to what extent the variations of the molecular conductivity of lithium nitrate solutions with the composition of the solvent can be ascribed to changes (1) in the coefficient of ionisation, (2) in the fluidity of the solution, and (3) in the aggregation of solvent particles round the ions.

Discussion.

Mr. Dunstan pointed out that some misconception had evidently arisen in the minds of the authors as to the curves published by

Messrs. Thole, Hunt, and himself (*Trans.*, 1907, **91**, 1728). For the purpose of more clearly representing the composition of the hydrates of pyridine, the tangents to the curves at the points of flexure were produced, and this gave rise to the erroneous impression that the curves were built up in sections. He also drew attention to the fact that every such "discontinuity" in the density curve was repeated in the viscosity curve, and instanced the work of Pickering in support of the contention that such hydrates do exist in solution.

Mr. R. J. CALDWELL agreed with the authors that the usefulness of most previous work on strong solutions is impaired by the fact that "volume normal" solutions have been employed instead of solutions made up by weight. He had already measured electrical conductivities of solutions made up by weight, taking account of the density, as the authors appeared to have done.

The specific rotatory power of sucrose varied from 66·5° in pure water to 83·8° in pure pyridine, but until the concentration of the pyridine reached 30 per cent. the rotatory power did not vary much from the value obtained in pure water (Wilcox, *J. Physical Chem.*, 1901, **5**, 592). At low concentrations, the pyridine, existing doubtless in a hydrated condition, was prevented from exerting any influence on the dissolved sugar. The values obtained by the authors for the conductivity of lithium nitrate appeared to be entirely analogous, leading to the same conclusion with regard to the pyridine.

Mr. HARTLEY said that he did not believe in the existence of any irregularities in the density or viscosity curves, as the greater the care with which the determinations were made the more nearly did the experimental values lie on smooth curves. The determination of density was so much more accurate an operation than the determination of viscosity, that he did not think the anomalies in the viscosity curves could be explained by those in the density curves. In reply to Dr. Barger, he said that the authors recognised that pyridine possessed residual valencies, although the liquid molecules were probably unassociated, otherwise it would have no dissociating influence on salts dissolved in it.

*16. "The constitution of umbellulone. Part III."

By Frank Tutin.

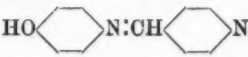
Semmler's recent statements (*Ber.*, 1907, **40**, 5017) respecting the constitution of umbellulone are based on experiments conducted with "β-dihydroumbellulone" and its derivatives. Since the material employed by Semmler consisted of highly impure umbellulone, there is no evidence in support of the assumption that "β-dihydroumbellulone" is a derivative of umbellulone, but, on the other hand, the experimental facts lead to the contrary conclusion.

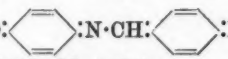
In addition to this uncertainty regarding the source of the preparation which had been called "β-dihydroumbellulone," this has now been shown to be a mixture, consisting chiefly of an unsaturated ketone, but also containing a saturated one, and it can only be from the latter that Semmler has prepared homotanacetonedicarboxylic acid.

Semmler's results, therefore, are devoid of significance in so far as they pertain to the constitution of umbellulone.

*17. "Colour and constitution of azomethine compounds." Part I. By Frank George Pope.

The nitrohydroxyazomethine compounds show an entirely different absorption spectrum from that of their alkali salts when the nitro- and hydroxyl groups are in the para-position to the azomethine group, and, from the similarity of the ·N:CH· grouping to the ·N:N· grouping in many respects, it would seem apparent that the alkali salts of these compounds could be formulated on a di-quinonoid basis, the free hydroxyl compounds being represented thus:



and the alkali salts as  (compare Hewitt and Mitchell, *Trans.*, 1907, **91**, 1251).

A similar state of things may also be observed, although to a slightly less extent as regards absorption, when the nitro- and hydroxyl groups are in the ortho- and para-positions to the azomethine grouping.

The following compounds were described: p-4-*nitrobenzylideneaminophenol*, m. p. 168·5°; o-4-*nitrobenzylideneaminophenol*, m. p. 161°; p-3-*nitrobenzylideneaminophenol*, m. p. 154°; o-3-*nitrobenzylideneaminophenol*, m. p. 135°; o-*hydroxybenzylidene*-m-*nitroaniline*, m. p. 132°.

Discussion.

Dr. Hewitt remarked that, whilst the general type of absorption was similar for corresponding azo- and azomethine compounds, replacement of a nitrogen atom by a methenyl group increased the oscillation frequency.

***18. "The preparation of *l*-benzoin."**
By Alexander McKenzie and Henry Wren.

l-Benzoin, obtained from *l*-mandelamide and magnesium phenyl bromide, melts at 131—132·5°, reduces Fehling's solution, and has $[\alpha]_D^{10.5}$ −118·6° for $c = 0{\cdot}9232$ in acetone solution.

DISCUSSION.

Dr. MCKENZIE, in reply to Dr. Lowry and Dr. Lander, stated that no racemisation, either partial or complete, had so far been observed with *l*-benzoin.

19. "Organic derivatives of silicon. Part V. Benzylethylsilicone, dibenzylsilicone, and other benzyl and benzylethyl derivatives of silicane." By Robert Robison and Frederic Stanley Kipping.

Benzylethylsilicone, BzEtSiO, prepared from benzylethylsilicon dichloride (Kipping, *Trans.*, 1907, **91**, 720), has little in common with benzyl ethyl ketone; it boils at 305—315° (22 mm.), is not reduced by various reagents, and gives neither an oxime nor a hydrazone; molecular weight determinations in acetic acid solution point to the formula $(BzEtSiO)_3$.

Benzylethylsiliconesulphonic acid is easily obtained by sulphonating the silicone with sulphuric acid; the *barium* salt, $(C_9H_{11}SiSO_4)_2Ba$, is soluble in water, but does not crystallise well.

Dibenzyl ethyl silicol, $Bz_2EtSi{\cdot}OH$, was obtained as an oil; it passes spontaneously into *dibenzylethylsilicyl oxide*, $(BzEtSi)_2O$, a crystalline substance melting at 54°.

Tribenzylsilicyl chloride, Bz_3SiCl, crystallises in prisms melting at 141°, and is decomposed by water, giving tribenzylsilicol.

Dibenzylsilicon dichloride, Bz_2SiCl_2, prepared from silicon tetrachloride and magnesium benzyl chloride, crystallises in massive prisms and melts at 50—52°; when decomposed with water, it yields a *hydrol* of the molecular formula, $Bz_2Si(OH)_2$, which crystallises in long, asbestos-like needles melting at about 101° (*α-hydrol*), and also an isomeric *hydrol*, which forms large, transparent prisms melting at about 75° (*β-hydrol*); the latter was recently described by Dilthey (*Ber.*, 1905, **38**, 4132). In some cases, only one of these hydrols is formed, and in others both are obtained, the *β*-isomeride predominating, but the conditions which determine their formation are unknown. Both hydrols pass into *dibenzylsilicone* (an oil) when they are heated,

and the β-compound is readily reproduced by treating this oil with water; the α-hydrol is not regenerated in this way. Both hydrols give termolecular *dibenzylsilicone*, $(Bz_2SiO)_3$ (m. p. 98°), when they are heated with acetic anhydride.

The experimental data do not yet afford any explanation of the existence and relationship of these isomeric hydrols.

20. "The residual affinity of the coumarins and thiocoumarins as shown by their additive compounds." By Arthur Clayton.

The coumarins and thiocoumarins combine with mercuric chloride, forming compounds of the type $R,HgCl_2$, where R is a coumarin or a thiocoumarin. This combination takes place with the following coumarins and their sulphur analogues: coumarin, 7-methylcoumarin, 4 : 7-dimethylcoumarin; 3 : 4 : 7-trimethylcoumarin, thiocoumarin, *7-methylthiocoumarin* m. p. 125—126°, 4 : 7-*dimethylthiocoumarin* m. p. 118—119°, and 3 : 4 : 7-*trimethylthiocoumarin* m. p. 124—125°. The thiocoumarins are prepared by the action of phosphorus pentasulphide on the corresponding coumarins, and, unlike the coumarins, yield oximes and phenylhydrazones.

Other oxonium compounds of the coumarins were described.

21. "The influence of foreign substances on certain transition temperatures and the determination of molecular weights." By Harry Medforth Dawson and Colin Gyrth Jackson.

The depression of the temperatures at which changes take place in certain condensed systems on the addition of foreign substances has been examined. The changes investigated were: (1) the conversion of sodium thiosulphate primary pentahydrate into the corresponding dihydrate at 48·1°; (2) the transformation of sodium bromide dihydrate into the anhydrous salt at 50·67°, and (3) the formation of tachhydrite ($CaCl_2,2MgCl_2,12H_2O$) from calcium and magnesium chloride hexahydrates at 22·40°.

Constants representing the depression of the transition temperature when 1 gram-molecule of the foreign substance is contained in 100 grams of the saturated transition solution have been calculated. From a knowledge of these constants, the corresponding invariant points may be utilised for the purpose of obtaining the molecular weights of dissolved substances.

22. "The bromination of *p*-hydroxydiphenylamine."
By Alice Emily Smith and Kennedy Joseph Previté Orton.

The bromination of *p*-hydroxydiphenylamine is rendered difficult by the readiness with which oxidation to a quinoneanil, $Ar{\cdot}N{:}C_6H_4{:}O$, is effected. All attempts to prepare mono- or di-bromo-derivatives failed, a tribromo-compound apparently being the primary product of bromination. It is a very remarkable fact that isomeric tri- and tetra-bromo-derivatives are not formed, the successive entrance of the bromine atoms following a single definite course.

The *tri-*, *tetra-*, *penta-*, *hepta-*, and *octa-bromo*-p-*hydroxydiphenylamines*, and the corresponding *benzoxy*-derivatives and *quinoneanils* (*phenyliminoquinones*) were described.

23. "The decomposition of ammonium dichromate by heat."
By William Marrs Hooton.

It is generally stated that ammonium dichromate on ignition decomposes quantitatively into nitrogen, water, and chromium sesquioxide; but Darby, in 1849, pointed out that a little ammonia was always liberated, and the author has found that the gaseous products of decomposition in air or in a vacuum always contain appreciable amounts of oxygen and oxides of nitrogen. Moreover, the solid residue is not homogeneous; it contains dark brown flakes, and evolves water when heated to bright redness.

If, instead of igniting the salt, it is decomposed slowly by heating it in air below its ignition temperature (190°) until the weight is constant, atmospheric oxygen takes part in the change. The final product is a hydrated form of chromium dioxide, having the composition $2CrO_2,H_2O$. It is a glistening, black powder, which on being strongly heated yields oxygen, water, and chromium sesquioxide without incandescence. When heated with hydrochloric acid, chlorine is freely evolved. When boiled with potassium hydroxide solution, it yields potassium chromate and chromium hydroxide.

If ammonium dichromate is heated below its ignition temperature in a vacuum or in absence of oxygen, the final product is a dull greenish-black powder having the composition $H_2Cr_2O_4$. This is not a hydrated form of chromium sesquioxide, for it incandesces brightly when heated to 400°. Even after boiling with water, filtering, and drying, it still incandesces when heated to 400°. During incandescence, water is formed, but no gas is liberated, and the sesquioxide formed is not bulky. This compound is not acted on by boiling potassium hydroxide solution, and only slowly by hot hydrochloric acid, no chlorine being evolved.

24. "The effect of constitution on the rotatory power of optically active nitrogen compounds. Part II." By Humphrey Owen Jones and John Robertshaw Hill.

The authors have resolved a set of five optically active nitrogen compounds, and have determined the rotatory powers of the basic ions (compare *Trans.*, 1906, **89**, 282).

The compounds contain the *p*-bromophenyl, methyl, and allyl groups with one of the homologous groups, ethyl, *n*- or *iso*-propyl, *iso*butyl, or *iso*amyl, and differ from those, forming one of the sets already described only in the replacement of one of the hydrogen atoms of the phenyl group by bromine.

The *n*-propyl, *iso*butyl, and *iso*amyl compounds were resolved by means of *d*-bromocamphorsulphonic acid, the *iso*propyl compound by means of *d*-camphorsulphonic acid, and the ethyl compound by means of *d*-tartaric acid. The following table summarises the results obtained:

	Melting point of iodide.	Molecular rotatory power of ion at 15°.	Molecular rotatory power of iodide in alcohol.
Ethyl	142—143°	− 31°(?)	− 20°
n-Propyl	142—143	+141	+144
*iso*Propyl	153	+161	+165
*iso*Butyl	133—134	+ 96	+117
*iso*Amyl	135—136	+ 94	+111

The rotatory power of the iodide in chloroform was determined when possible, and was found to be greater than in alcohol; autoracemisation of the iodide occurred in chloroform in all cases.

The maximum rotatory power is found in the propyl compounds just as in the set of unbrominated compounds, also the rotatory power of this set of compounds, with the exception of the ethyl compound, is considerably greater than that of the unbrominated set.

25. "Malacone, a silicate of zirconium." By Alexander Charles Cumming.

The author finds that the formula ZrO_2,SiO_2 corresponds more closely with the observed composition of malacone than does the formula $3ZrO_2,2SiO_2$ assigned to it by Kitchin and Winterson (*Trans.*, 1906, **89**, 1568).

A detailed examination gave no reason to suspect the identity of the zirconia, or to suspect the presence of an unknown impurity. The presence of argon cannot be explained by the presence of any new radioactive element, as the radioactivity can be sufficiently accounted for by the presence of radium.

26. "The reducibility of magnesium oxide by carbon." By Roland Edgar Slade.

The isolation of magnesium by direct reduction of the oxide by carbon has been effected at temperatures above 1700°, and the chief hindrance to the preparation of the metal by this reaction has been found to be due to the back reaction which occurs at lower temperatures between magnesium and carbon monoxide.

Various methods were adopted for removing the metal from contact with the carbon monoxide. Rapid evacuation of the vessel in which the reaction occurs, absorption of the magnesium by molten copper, and reduction of magnesia in presence of aluminium, or in a swift stream of hydrogen, have all proved successful.

27. "The crystal form of halogen derivatives of open-chain hydrocarbons with reference to the Barlow-Pope theory of structure." By Frans Maurits Jaeger.

The author has determined the crystalline forms of a number of halogen derivatives of open-chain hydrocarbons, such as tetrabromo-$\beta\beta$-dimethylpropane, 1:3:5-hexatriene, di- and tetra-bromide and tetra-iodoethylene, for the purpose of ascertaining whether predictions concerning their crystalline form, based on the theory of Barlow and Pope, are justified by the experimental results. In accordance with the indications of the theory, it is found that the substances named above exhibit a close morphotropic relationship. The theory also allows of the prediction that tetrabromo-$\beta\beta$-dimethylpropane should be represented by a pseudo-cubic assemblage; actually it is found that, although the compound crystallises in the monosymmetric system, it is pseudo-cubic.

28. "The determination of the rate of chemical change by measurement of the gases evolved." By Francis Edward Everard Lamplough.

Further work on the above subject has confirmed the results given in a former communication (*Proc.*, 1906, **22**, 280), with the exception of the paragraph referring to the decomposition of ammonium nitrite.

A few experiments have been performed on the action of sodium hypochlorite on carbamide. The rate of evolution of gas does not give results which can be interpreted by a simple law, owing to the complexity of the reaction; the velocity of the reaction, as measured

by the rate of evolution of gas, rises to a maximum and then diminishes.

The reaction between nickel carbonyl and iodine has been found to be of a complex nature, even in cases where either reagent is in considerable excess. When the nickel carbonyl is present in great excess, a remarkable phenomenon is met with, the action proceeding in a steady manner until a point is reached at which it abruptly terminates almost without warning.

29. "The temperatures of spontaneous crystallisation of mixed solutions, and their determination by means of the index of refraction. Mixtures of solutions of sodium nitrate and lead nitrate." By Florence Isaac.

Previous experiments on simple solutions established a "supersolubility curve" which marks their temperatures of "spontaneous" crystallisation.

The supersolubility curve for a mixture of three constituents, sodium nitrate, lead nitrate, and water, has now been determined by measurement of the refractive indices.

In the first set of twenty-two experiments, the proportion of lead nitrate to water was kept constant as 3 : 10, whilst the amount of sodium nitrate varied; in the second set of seventeen experiments, the proportion of sodium nitrate to water was kept constant as 3 : 4, whilst the amount of lead nitrate varied.

In both cases, it was found that as the temperature of the liquid falls the refractive index rises to a maximum value. A few crystals usually appear in the supersaturated solution before the maximum index is reached, and at, or about, the maximum point spontaneous crystallisation sets in and gives rise to a dense shower of crystals.

In each set, these maximum points determine the "supersolubility" curve.

The two supersolubility curves may be regarded as plane sections of a supersolubility surface for all possible mixtures of the three constituents.

The curves of spontaneous crystallisation were also determined by experiments with the same solutions in sealed glass tubes. These cannot be made to crystallise until they have reached the temperature already determined from the refractive indices.

The solubility curves for these mixtures were also determined, and their relation to the supersolubility curves established.

30. "Contributions to the chemistry of the terpenes. Part III. Some oxidation products of pinene." By George Gerald Henderson and Isidore Morris Heilbron.

The acid $C_9H_{15}CO_2H$, obtained from pinene as previously described (Henderson and Gray, Trans., 1903, **83**, 1299), could not be brominated directly, but was converted into its *chloride*, a viscous, colourless oil. When heated with bromine, this yields the *chloride* of a *bromo-acid*, $C_9H_{14}Br{\cdot}COCl$, an oily liquid, from which, with water, the *bromo-acid*, $C_9H_{14}Br{\cdot}CO_2H$, was obtained. This is a crystalline solid, and when boiled with aqueous sodium carbonate yields the *hydroxy-acid*, $C_9H_{14}(OH){\cdot}CO_2H$, crystallising from water in colourless prisms. Its *sodium* salt is readily, and its *silver* salt very sparingly, soluble in water.

In preparing the bromo-acid, a small quantity of a crystalline, neutral *compound*, apparently of the composition $C_{10}H_{13}OBr$, separated. Along with the hydroxy-acid there was also obtained a small amount of another *acid*, probably of the formula $C_{10}H_{14}O_2$, which is crystalline and insoluble in water. Its *silver* salt crystallises from water in colourless needles.

The ketone previously described (*loc. cit.*) has now been obtained in a pure state, and has the formula $C_9H_{14}O$. On reduction, it yields the *alcohol*, $C_9H_{15}{\cdot}OH$, a colourless, oily liquid, from which a *phenylurethane* and an *acid phthalic ester*, both crystalline solids, have been prepared.

When heated with ammonium formate, the ketone is converted into the formyl derivative of an *amine*, $C_9H_{15}{\cdot}NH_2$, which is a colourless liquid with a disagreeable odour, and is almost insoluble in water. Its *hydrochloride*, which is extremely easily soluble in water, crystallises in silky needles, and its *platinichloride* in pale yellow leaflets.

The chlorinated oxidation product which is separated during the purification of the ketone is a white, crystalline solid of formula $C_{10}H_{15}OCl$. It is slowly decomposed when heated with alcoholic sodium ethoxide, and yields a colourless, crystalline compound, which does not contain chlorine and has a penetrating odour.

31. "A β-lactonic acid from acetone and malonic acid." By Andrew Norman Meldrum.

When malonic acid and acetone are mixed with acetic anhydride and a little sulphuric acid, the malonic acid dissolves, and after twenty-four hours a new, crystalline acid is obtained, which melts at 97° and decomposes at a higher temperature. The composition and the molecular weight (determined by the boiling-point method) lead to the formula $C_6H_8O_4$.

The substance is saturated; it decomposes easily, under various conditions, into acetone and malonic acid (or, in place of malonic acid, carbon dioxide and acetic acid), and when heated with aniline it gives acetone, carbon dioxide, and acetanilide.

Since the acid is monobasic and yields the salts:

$$C_6H_7O_4Ag,\ C_6H_7O_4Na,\ C_6H_7O_4K,H_2O,$$

it is evidently the *β-lactone* of *β-hydroxyisopropylmalonic acid*, $\begin{matrix} CMe_2\cdot CH\cdot CO_2H \\ | \quad\quad | \\ O\text{——}C \end{matrix}$.

ERRATUM.

1908, p. 3, line 14 from below, *for* "$2TeO_2\cdot HNO_3$" *read* "$2TeO_2,HNO_3$."

At the next Ordinary Meeting, on **Thursday**, February **20th**, 1908, at **8.30** p.m., there will be a Ballot for the election of Fellows, and the following papers will be communicated:

"The action of thionyl chloride and of phosphorus pentachloride on the methylene ethers of catechol derivatives." By G. Barger.

"The preparation of conductivity water." By H. Hartley, N. P. Campbell, and R. H. Poole.

"Derivatives of *p*-diazoiminobenzene." By G. T. Morgan and Miss F. M. G. Micklethwait.

"A study of the diazo-reaction in the diphenyl series." By G. T. Morgan and Miss F. M. G. Micklethwait.

"Organic derivatives of silicon. Part VI. The optically active sulphobenzylethylpropylsilicyl oxides." By F. S. Kipping.

"A simple manometer for vacuum distillation." By N. L. Gebhard.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

The following Candidates have been proposed for election. A ballot will be held on Thursday, February 20th, 1908.

Andreae, Edward Philip,

"Crestalba," Champion Hill, S.E.

Chemist. Ph.D. (Berlin). Dissertation: "Ueber Chitonsäure u. Chitarsäure." Ueber die Einwirkung von Diaethylmalonylchlorid auf Einige Diamine.

R. W. Sindall. R. H. Aders Plimmer.
Otto Oberländer. E. Frankland Armstrong.
J. C. Cain.

Barr, Guy,

79, Fillebrook Road, Leytonstone, N.E.

Assistant in the Chemical and Metallurgical Department, National Physical Laboratory. Scholarship at Christ's College, Cambridge, 1903. B.A. of Cambridge. First Class in both parts of Natural Sciences Tripos: Pt. I, 1906; Pt. II (Chemistry), 1907. B.Sc. of London; Honours in Chemistry, Second Class, 1907. With Dr. H. J. H. Fenton, paper: "Colour Reactions of some Organic Acids," Cambridge Philosophical Society, 1907.

W. J. Sell. H. O. Jones.
H. J. H. Fenton. C. T. Heycock.
G. D. Liveing.

Barton, Robert, junior,

48, Wellclose Mount, Leeds.

Analytical Chemist. Four (4) years as Pupil and Assistant to

Mr. T. Fairley, F.I.C., F.C.S., City and County Analyst, Leeds. Three (3) Sessions at the late Yorkshire College, Leeds. Three and a-half (3½) years, Assistant Chemist with Messrs. Lever Bros., Ltd., Port Sunlight, Cheshire. At present, Assistant to Mr. G. W. Slatter, A.R.C.Sc., F.I.C., F.C.S., Northern Counties Laboratories, Dock Street, Leeds.

G. W. Slatter. B. A. Burrell.
Thomas Fairley. J. B. Cohen.
Arthur Smithells. *W. Lowson.*

Braun, Marie Joseph Arsène, Ph.D.,
5, Aspinall Road, Brockley, S.E.

Chemist at the South Metropolitan Gas Co. Technical and scientific diplomas of the "Städtische Chemieschule" at Mülhausen i/Els. 1897—98 Assistant to Prof. E. Noelting at the same school. Ph.D., Basle, 1899. 1899—02 Assistant to Dr. J. Tcherniac at Freiberg, i/Br. 1902—04 Chemist at the "Fabriques de Produits Chimiques" at Mülhausen i/Els. 1904 to present date at the South Metropolitan Gas Co. Publications: "Weitere Untersuchungen über die Bildung von Indazolen," Thesis, Basle, E. Birkhäuser; "Einige Derivate des Acetophenons," Thesis, Basle, E. Birkhäuser; E. Noelting, A. Braun, and G. Thesmar: "Nitro- und Brom-derivate der Xylidine," *Ber.*, **34**, 2242; H. Rupe, A. Braun, and K. von Zembruski: "Ueber einige Abkömmlinge des Acetophenons," *Ber.*, **34**, 3522; A. Braun and J. Tcherniac "Ueber die Produkte der Einwirkung von Acetanhydrid auf Phthalamid," *Ber.*, **40**, 2709.

J. Tcherniac. Edward Evans.
Otto Oberländer. *J. C. Cain.*
R. W. Sindall.

Brown, Harry James,
Pembrey Lead Works, Burry Port.

Assayer and Analytical Chemist (at present Chemist to Messrs. Rowe Bros. & Co., Ltd., and Manager of their White Lead Works). Received training at J. S. Merry & Co.'s Assay Office, Swansea, 1888—1891. Assistant Chemist to Elliotts Metal Co., Ltd., 1891—1897. Established Assay Offices and Ore Purchasing Yards for E. M. Co., Ltd., in Mexico and Spain, 1897—1899. Chemist to "Otavi Mining Expedition," G.S.W. Africa, 1900—1901. Engaged as above from 1902 to date. Honours Certificates in Chemistry and Metallurgy (S. K.), and Teacher for three years.

Clarence A. Seyler. T. C. Davison.
W. R. Bird. F. W. Harris.
Basil Wm. Valentin.

Brown, Walter, jun.,
Brookvale, Strathaven, N.B.

Analytical Chemist. Studied Chemistry first under J. McCutcheon, F.C.S., Lecturer in Chemistry to the County of Lanark. Served two years' Chemical Apprenticeship to Prof. J. R. Watson, obtaining Elem. and Adv., Theor. and Prac. Science and Arts Cert. in Organic and Inorganic Chemistry; followed by two years in the University of Leipzig. For over two years Chief Assistant to Prof. J. R. Watson, Public Analyst for Irvine, &c.; also taking active part in Saturday Classes for Teachers and Contin. Classes, held at Anderson's College, Glasgow. Since January, 1907, Chemist (temporary) responsible for all analytical work in the Public Health Laboratory of the County of Lanark.

James McCutcheon. Fred. D. S. Robertson.
Frank W. Young. H. T. Calvert.
John Glaister.

Carpenter, John Arthur,
New College, Oxford.

Demonstrator in Chemistry. Scholar of New Coll., Oxford; at present Demonstrator, Christ Church, Oxford. First Class London Int. Sci., 1907, in Chemistry and Physics. First Class Honour Moderations (Maths.), Oxford, 1904. First Class Final Honours Chemistry, 1906. Second Class Final Honours Physics, 1907. Bachelor of Arts.

H. Brereton Baker. Allan F. Walden.
Andrea Angel. D. H. Nagel.
W. H. Lewis.

Clarke, Hans Thacher,
Gayton Corner, Harrow.

Chemist. Chemical Student, University College, London.

J. Norman Collie. Samuel Smiles.
William Ramsay. Edward C. Cyril Baly.
N. T. M. Wilsmore.

Collier, William Henry,
13, Powis Gardens, Bayswater, W.

Teacher of Chemistry. Int. B.Sc. (London University). Teacher at Regent Street Polytechnic (5 years). Six years at College and on the staff of the Merchant Venturers' Technical College, Bristol. Working for B.Sc. exam. of London Univ. (Honours Deg. in Chemistry). Joint

author with H. R. Ellis, F.C.S., B.Sc., of paper submitted to Chem. Soc. last month.

J. C. Crocker. Frank E. Weston.
H. R. Ellis. F. H. Lowe.
J. B. Coleman.

Crichton, David Cowan,

Backhill House, Musselburgh.

Manager to Caledonian Portland Cement Co., Cousland, Dalkeith. Degrees held: Master of Arts (St. Andrews); Bachelor of Science (St. And.); Associate of the Institute of Chemistry (London). Papers published: "Electrolysis of Potassium Ethyl Dipropylmalonate" (*Journal of Chem. Soc.*); "Alkyl Ammonium Hydrates" (*Journal of Chemical Society*).

James Walker. J. H. Wigner.
John S. Lumsden. John Foggie.
Charles Spackman.

Dickinson, Cyril,

"Abbotsford," Hollycroft Avenue, Hampstead.

Analytical Chemist. B.Sc. (Vict. and Leeds); F.I.C. Three years under Prof. Smithells at Leeds University. Assistant Chemist, Bradford Dyers' Association. Head Assistant to J. Kear Colwell, Esq., F.I.C., F.C.S.; at present Senior Assistant to Dr. W. Scott Tebb (Borough Analyst for Southwark), with whom I have been for the last 4 years.

Arthur Smithells. J. Kear Colwell.
J. B. Cohen. H. D. Law.
F. Mollwo Perkin.

Eagles, Edwin Mortimer, M.A. Cantab.

5, Winsham Grove, Clapham Common, S.W.

Senior Science Master, Battersea Grammar School (since Easter, 1902). Eight years Science Master, Central Foundn. School of London; 10 years Head of Science Dept., Willesden Polytechnic. In conjunction with Mr. M. M. Pattison Muir, I carried out original work on "Thiohaloid Compounds of Bismuth" (*Jour. Chem. Soc.*, 1895).

M. M. Pattison Muir. A. Hutchinson.
Kennedy J. P. Orton. *A. E. Bellars.*
S. Ruhemann. *H. J. H. Fenton.*

Gale, Robert Cecil,

38, Scarsdale Villas, Kensington.

Student. Advanced Student of Chemistry at the Central Technical College, Exhibition Road, S.W.

Henry E. Armstrong. Gerald T. Moody.
William A. Davis. William Robertson.
T. Martin Lowry.

Heron, John Maxwell,

North House, Manningtree, Essex.

Brewers' Chemist. Chemist to Messrs. Free, Rodwell & Co., Maltsters, Mistley, Essex. Seven years Assistant to John Heron, 110, Fenchurch Street. Last three years Chemist to Messrs. Hole & Co., Castle Brewery, Newark-on-Trent.

Horace T. Brown. John Heron.
Leonard Temple Thorne. Chas. Geo. Matthews.
George Harrow.

Hilditch, Thomas Percy,

4, Park Hall Place, East Finchley, N.

Research Student and Demonstrator, University College, London. Student for three years and Demonstrator in Chemistry for the past two sessions at University College. Have published several papers in the Society's Journal in conjunction with Prof. J. N. Collie, Dr. S. Smiles, and Mr. A. E. Dunstan.

William Ramsay. N. T. M. Wilsmore.
J. Norman Collie. A. W. Stewart.
Edward C. Cyril Baly. A. E. Dunstan.
Samuel Smiles. P. C. Austin.

Merrick, Arnold,

66, Rothbury Terrace, Newcastle-on-Tyne.

Schoolmaster. Teaching Chemistry and Physics. Late Johnston Scholar, University of Durham (College of Science, N/C).

P. Phillips Bedson. S. Hoare Collins.
F. C. Garrett. Herbert Blair.
J. T. Dunn.

Morewood, Capel Darcy,

Ferndale, Frodingham, Doncaster.

Analytical Chemist. I was engaged from February to May, 1906, in Metallurgical and Analytical work in Mr. Seyler's Laboratory, Swansea, where I paid special attention to the micrographic examina-

tion of iron and steel. From June to December, 1906, I was on the staff of Messrs. Ed. Riley, City Road, London. From then till now, I have been in entire charge of the laboratory at Lord St. Oswald's Ironstone Mines, Frodingham.

John W. Bevan. Edwd. Riley.
Clarence A. Seyler. *F. J. Bloomer.*
Carl Langer.

Oke, Alfred William, B.A., LL.M., F.G.S., F.L.S. (Trinity College, Cambridge).

32, Denmark Villas, Hove, and Orielton, Highfield Lane, Southampton.

Solicitor. Worked at Cambridge University Laboratory. Am anxious to keep up my knowledge and interest in the subject and its developments.

Alfred C. Young. W. J. A. Butterfield.
J. Brierley. *W. J. Sell.*
H. J. H. Fenton.

Pingriff, George Neville,

39, Hall Road, Handsworth, Staffs.

Chemistry master at the Central Secondary School, Birmingham. Above and similar temporary post at Wyggeston School, Leicester. 1st Class Natural Science Tripos, Part I., Cambridge, 1906; 2nd Class Natural Science Tripos, Part II., Chemistry, 1907.

F. H. Neville. W. J. Sell.
H. J. H. Fenton. H. O. Jones.
Lionel M. Jones.

Pinnock, Douglas Robert,

"St. Patrick's," 31, The Gardens, E. Dulwich, S.E.

Student. Advanced Student in Chemistry at the City and Guilds College, S. Kensington.

Henry E. Armstrong. Gerald T. Moody.
William Robertson. William A. Davis.
Robert J. Caldwell.

Runeckles, Arthur Robert,

68, Kyrle Rd., New Wandsworth, S.W.

Advanced Student in Chemistry at the Central Technical College, S. Kensington. Clothworkers' Scholar and Bancrofts' Exhibitioner.

Henry E. Armstrong. Gerald T. Moody.
William A. Davis. Robert J. Caldwell.
T. Martin Lowry.

Scott, Andrew L.,

Fir Lodge, Cheshunt, Herts.

Analytical Chemist. Official Address: Royal Gunpowder Factory, Waltham Abbey, Essex. Assistant to R. R. Tatlock, Esq., F.R.S.E., &c.; Assistant to Benedict Kitto, Esq. F.I.C., &c. Chemist in Charge of Nitroglycerine Department, Royal Gunpowder Factory. Fellow of the Institute of Chemistry.

Wm. Rintoul.	Geo. W. MacDonald.
R. R. Tatlock.	Wm. T. Thomson.
R. T. Thomson.	G. H. Welsford.
J. A. Williamson.	*John Shields.*

Shaw, William Bayliss,

Lonsdale House, Walsall.

Undergraduate. Student of Chemistry in the University of Oxford.

W. W. Fisher.	Allan F. Walden.
John Watts.	F. L. Overend.

J. E. Marsh.

Smythe, John Armstrong,

15, The Poplars, Gosforth, Newcastle-on-Tyne.

Lecturer in Chemistry, Armstrong College, Newcastle. Author of following papers: "Ueber das Nitrosopinen," *Inorg. Diss. Göttingen*, 1898. "The Bases contained in Scottish Shale Oil" (with F. C. Garrett), Part I., *Journ. Chem. Soc.*, **81**, 449; Part II., *Journ. Chem. Soc.*, **83**, 763, and of others connected with Chemical Geology.

P. Phillips Bedson.	S. Hoare Collins.
F. C. Garrett.	Herbert Blair.

J. T. Dunn.

Spiers, Charles Sedgley,

The Woodlands, Scalford Road, Melton Mowbray.

Chemist. Interested in chemical manufactures, and anxious to keep in touch with the latest chemical research. Member of the Pharmaceutical Society, and have studied Science under Mr. F. A. Hillard, B.A. (late Wyggeston Grammar School), and the late Mr. Watson-Will, F.C.S., Metropolitan College of Pharmacy.

Harry Lucas.	F. Filmer De Morgan.
David J. Williams.	*Frederick B. Power.*

Thomas Tyrer.

Stead, Arthur,

113a, Kellner Street, Bloemfontein, O.R.C.

Assistant to Govt. Analyst and Bacteriologist of the O.R.C. since Oct., 1904; Senior Norfolk County Council Scholarship (1895—

1900); B.Sc. (Victoria). First Class Ordinary Degree in Chemistry and Physics, and "Studentship," Univ. College, Liverpool, 1899. Education Department, Heidelberg, Transvaal, 1902—1904.

J. Campbell Brown. J. Handby Ball.
A. W. Titherley. John S. Smythe.
W. Collingwood Williams.

Trechmann, Adolph Octavius,
The Old Palace, Rochester,

Cement Manufacturer. Studied Chemistry under Sir Henry Roscoe and Professor Dixon at Owens College from 1884—1888. Managing Director of the Cement Works of Trechmann, Weekes & Co., Limited, of Halling, near Rochester, Kent. A member of the Society of Chemical Industry since 1888.

Alfred Gordon Salamon. Thos. Tyrer.
Arthur W. Crossley. Boverton Redwood.
Walter F. Reid. *Louis J. Riley.*
William Ramsay.

Tyson, Thomas Marshall,
99, Sebert Road, Forest Gate, E.

Analytical Chemist in a works laboratory. I have had three years' training under Mr. J. S. Remington, Aynsome Analytical and Technical Laboratories. Mr. Remington then engaged me as an Assistant at his laboratories, and finally got me my present position as Works Chemist. I am also continuing my studies at the West Ham Technical Institute night classes.

John Stewart Remington. W. Ormston Young.
Claude Smith. *George Dean.*
F. Henry Streatfeild.

Unwin, Harry Jackson,
Market Place, Clay Cross, nr. Chesterfield.

Science Teacher. Laboratory Assistant and Teacher of Chemistry for 8 years in Secondary Schools. Trained at Royal College of Science. South Kensington Certificates: Adv. Prac. Inorg. Chemistry, 1st Class; Adv. Theor. Inorg. Chemistry, 1st Class.

Fredk. Cowling. W. E. Jennings.
A. H. Salway. *Harold Rogerson.*
Frank Tutin.

Wade, Alfred,
Fiji.

Government Pharmacist. For six years with Messrs. Reynolds & Branson, Leeds, Scientific Apparatus Manufacturers, &c. Passed

Minor Examn. (Pharmaceutical Society), 1903, and Major in 1904. Certificate of Honour and Silver Medal for Chemistry, 1904—6. Assistant Manager and Analyst to Messrs. Willows, Francis, Butler, and Thompson, Ltd., Manufacturing Chemists. Now Government Pharmacist, Fiji.

W. Palmer Wynne. — Frank Wade.
F. W. Branson. — *Thomas Fairley.*
J. H. Gough. — *B. A. Burrell.*

Walker, Herbert,

"Whyttington," Station Road, Wealdstone, N.W.

Civil Engineer and Surveyor to the Urban District Council, Wealdstone. Course of Study at Midland Institute, Birmingham, and at Mason's College, Birmingham. Science Teacher at Technical School, Corporation of Smethwick.

William A. Colebourn. — J. Wilson.
C. Sordes Ellis. — *J. Hart-Smith.*

Frank E. Weston.

Watson, Herbert Edmeston,

Tringhurst, Cranes Park, Surbiton.

Research Student at University College. Demonstrator 2 years at University College. B.Sc.; 1st Class Honours in Chemistry.

William Ramsay. — Samuel Smiles.
Edward C. Cyril Baly. — N. T. M. Wilsmore.

A. W. Stewart.

Watson, John,

5, Kendrew St., Darlington.

Science Teacher. Bachelor of Science (Armstrong College, Newcastle). Assistant Lecturer in Agricultural Chemistry, Armstrong College, Newcastle.

P. Phillips Bedson. — S. Hoare Collins.
F. C. Garrett. — Herbert Blair.
G. P. Dodds. — *W. F. Keating Stock.*

J. W. Patterson.

Williams, David Thomas,

9, Calvert Terrace, Swansea.

Analytical and Metallurgical Chemist. Student and Assistant Chemist for 5 years at Landore Iron & Steel Wks. (now Baldwin's, Ltd.). Fifteen years at Messrs. Elliott's Metal Co., Burry Port, the last six years of which as Chief Chemist. Honours Certificate S. K. Chemistry and Metallurgy, and had charge of Technical Classes for

4 years. Contributed note on "Estimation of Vanadium" (*Soc. Chem. Indus.*, 1902).

Clarence A. Seyler. Arthur C. Claudet.
T. C. Cloud. Frank B. Last.

F. W. Harris.

Williams, Joseph Henry,

"The Briars," 27, Canbury Avenue, Kingston-on-Thames.

Assistant Manager of Chemical and Pharmaceutical Laboratories Late Assistant to A. E. Bell, Esq., F.I.C. Member of the Pharmaceutical Society. Author of "Note on the Solubility of β-Eucaine Hydrochloride"; "An Important Method for the Preparation of Alcoholic Extracts." (Both of these papers were published in the *Pharmaceutical Journal.*)

Albert E. Bell. Francis Henry Wall.
John B. Tillott. William Robertson.

T. W. Firth Clark.

Wilson, Harry Percy,

3, Audley Rd., Colchester.

Science Superintendent, Technical and University Extension College, and Senior Chemical Lecturer, Colchester. Lecturer and Teacher of Analytical Chemistry, chiefly inorganic work connected with the engineering industry of Colchester, and with the gases required for gas-engines.

Arthur W. Nunn. Jos. Cowper.
J. Cardew Bedwell. *T. B. Wood.*

J. E. Purvis.

Withey, William Henry,

Stroud, Glos.

B.A. (Cantab.); 1st Class Honours, Part I, Natural Sciences Tripos (1905); 2nd Class Honours, Part II, do. (Chemistry), 1906. For twelve months in laboratory of Dr. S. Rideal, F.C.S., F.I.C.

W. J. Sell. H. J. H. Fenton.
Samuel Rideal. H. O. Jones.

G. Nevill Huntly.

Wood, Francis Charles Benjamin,

Deurne, near Antwerp, Belgium.

Technical Chemist. At present managing Dye Works. Student Royal Technical Institute, Salford, for 2—3 years; Chemist and Colourist at Leopold, Cassella and Co., Frankfort. Wishes to remain in contact with current English chemical literature.

J. R. Appleyard. E. J. Wilkinson.
E. Clark. *Ad. Liebmann.*
B. Prentice. *J. C. Cain.*

Yates, Joseph,

18, Park Street, Haslingden, Lancs.

Lecturer in Chemistry. Certificate in Applied Chemistry, Owens College, Manchester, 1899. Joint author of following papers: "Action of Aluminium Chloride on Camphoric Anhydride," *Trans.*, 1901, 1373; "Brazilin and Hæmatoxylin," *Trans.*, 1901, 1373, *Trans.*, 1902, 235; "Optically Active Reduced Naphthoic Acids," *Trans.*, 1906, 1101; "Relative Catalytic Effect of Bases on Optically Active Reduced Naphthoic Acids," *Trans.*, 1906, 1484.

Harold B. Dixon. Robert H. Pickard.
W. H. Perkin. J. F. Thorpe.

W. E. Bickerdike.

The following Certificates have been authorised by the Council under Bye Law I (3):

Collens, Archibald Edgar,

Port of Spain, Trinidad, B. W. Indies.

Laboratory Assistant and Chemical Demonstrator, Government Laboratory, Trinidad. Permanently employed at the Government Laboratory from March, 1900. Lecturer on Agricultural Science to Government Training Colleges from July 1, 1902, to March 31, 1905. Acting Science Master to Queen's Royal College, St. Mary's College, and Government Training Colleges from March 8, 1906, to June 12, 1906; and from August 27, 1907, continuing. Acting Professor of Chemistry to Queen's Royal College and St. Mary's College from September 11, 1907, to October 26, 1907. Acting Assistant Analyst, Government Laboratory, from August 14, 1904, to November 22, 1904; and from March 8, 1906, to June 12, 1906. Foreign Member, American Chemical Society (elected April, 1906).

P. Carmody. Joseph de Verteuil.

John G. Ferrier.

Francies, Joseph Valentine,

Sibpur, Calcutta, India.

Head Master, Civil Engineering College, and Lecturer in Chemistry. Instructor in Science, &c., Thomason C. E. College, Roorkee, from 1897 to 1905. Lecturer in Chemistry, C. E. College, Calcutta, since 1905.

E. R. Watson. P. P. Phillips.
Paul Brühl. *J. A. Cunningham.*

Singh, Puran,

Dehra Dun, India.

Acting Imperial Forest Chemist. Member of the Pharmaceutical and Chemical Societies of Japan. Late Research Scholar of Dr. Wilhelm Nag Nagai, Ph.D. (Berlin). Author of "Researches on Cantharidine—its extraction and determination" and "The Estimation Catechin." Acting Imperial Forest Chemist to the Government of India.

M. C. Nanjunda Row. *M. Goolab Roy.*

R. CLAY AND SONS, LTD., BREAD STREET HILL, E.C., AND BUNGAY, SUFFOLK.

Issued 28/2/08

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 24. **No. 337.**

Thursday, February 20th, 1908, at 8.30 p.m., Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

The PRESIDENT announced that letters have been received from those gentlemen recently elected Honorary and Foreign Members, acknowledging the honour which the Society desired to pay them.

Certificates were read for the first time in favour of Messrs. :

Albert Edward Findley, B.Sc., 1, Welford Road, Handsworth, Birmingham.
George Edward Holden, 23, Durnford Street, Middleton, Manchester.
Percy Hulme Hornby, 111, Nine Elms Lane, S.W.
Herbert Mansfield, B.Sc., A.I.C., 70, Stapleton Hall Road, Stroud Green, N.

Certificates have been authorised by the Council under Bye-Law I (3) in favour of Messrs. :

Bidhu Bhushan Dutt, M.A., Presidency College, Calcutta.
Atul Chandra Gañguli, B.A., Ravenshaw College, Cuttack, India.
Arthur Horrobin, Ajmer, Rajputana, India.
Pañchānan Neogi, Rajshahi College, Rajshahi, Bengal.

It was announced that the following changes in the Officers and Council were proposed by the Council:

Vice-Presidents to retire: Prof. A. Smithells and Prof. W. P. Wynne.

Ordinary Members of Council to retire: Mr. E. C. C. Baly, Dr. Bernard Dyer, Mr. E. Grant Hooper, and Dr. G. T. Moody.

As President: Sir William Ramsay.

As Vice-Presidents who have filled the office of President: Prof. H. E. Armstrong, Prof. A. Crum Brown, Sir William Crookes, Sir James Dewar, Dr. A. G. Vernon Harcourt, Prof. R. Meldola, Dr. H. Müller, Prof. W. Odling, Prof. J. Emerson Reynolds, Sir Henry E. Roscoe, Dr. W. J. Russell, Prof. T. E. Thorpe, and Prof. W. A. Tilden.

As Treasurer: Dr. Alexander Scott.

As Secretaries: Dr. M. O. Forster and Prof. A. W. Crossley.

As Foreign Secretary: Dr. Horace T. Brown.

As Vice-Presidents: Prof. J. Campbell Brown, Prof. J. J. Dobbie, Prof. F. S. Kipping, Dr. R. Messel, Sir A. Pedler, and Prof. W. H. Perkin.

As New Ordinary Members of Council: Mr. J. L. Baker, Mr. A. C. Chapman, Prof. J. B. Cohen, and Dr. J. T. Hewitt.

Dr. A. Harden, Dr. H. Forster Morley, and Dr. J. A. Voelcker were elected Auditors to audit the Society's Accounts.

A ballot for the election of Fellows was held, and the following were subsequently declared elected:

Edward Philip Andreae, Ph.D.
Guy Barr, B.A., B.Sc.
Robert Barton, jun.
Marie Joseph Arsène Braun, Ph.D.
Harry James Brown.
Walter Brown, jun.
John Arthur Carpenter, B.A.
Hans Thacher Clarke.
Archibald Edgar Collens.
William Henry Collier.
David Cowan Crichton, M.A., B.Sc.
Cyril Dickinson, B.Sc.
Edwin Mortimer Eagles, M.A.
Joseph Valentine Francies.
Robert Cecil Gale.
John Maxwell Heron.
Thomas Percy Hilditch.
Arnold Merrick.
Capel Darcy Morewood.
Alfred William Oke, B.A., LL.M.
George Neville Pingriff, B.A.
Douglas Robert Pinnock.
Arthur Robert Runeckles.
Andrew L. Scott.
William Bayliss Shaw.
Puran Singh.
John Armstrong Smythe.
Charles Sedgley Spiers.
Arthur Stead, B.Sc.
Adolph Octavius Trechmann.
Thomas Marshall Tyson.
Harry Jackson Unwin.
Alfred Wade.
Herbert Walker.
Herbert Edmeston Watson, B.Sc.
John Watson, B.Sc.
David Thomas Williams.
Joseph Henry Williams.
Harry Percy Wilson.
William Henry Withey, B.A.
Francis Charles Benjamin Wood.
Joseph Yates.

Of the following papers, those marked * were read :—

*32. "**Organic derivatives of silicon. Part VI. The optically active sulphobenzylethylpropylsilicyl oxides.**" By **Frederic Stanley Kipping.**

The sulphonic acids obtained by resolving *dl*-sulphobenzylethylpropylsilicyl oxide with one of the active methylhydrindamines (*Trans.*, 1907, **91**, 209) have been further studied, and the results clearly show that the two acids are optically active, enantiomorphously related compounds having the constitution

$$(SO_3H\cdot CH_2\cdot C_6H_4\cdot SiEtPr)_2O;$$

although they contain two asymmetric silicon groups, their specific rotations are very small, the values obtained for the sodium salts being $[\alpha]_D \pm 5{\cdot}8—5{\cdot}9°$.

The crystalline *dAdB*- and *lAlB*-methylhydrindamine derivatives differ very widely in outward properties from the *dAlB*- and *lAdB*-compounds, which have a very gelatinous or horny nature, but all four salts have a specific rotation $[\alpha]_D \pm 15—16°$ in methyl-alcoholic solution.

The *dAlB*- and *lAlB*-menthylamine salts are practically indistinguishable from one another or from the salt of the *dl*-acid, and this is also true in the case of the corresponding three *d*-bornylamine derivatives; the cinchonidine and cinchonidine hydrogen salts of the two active acids differ slightly in melting point.

dl-Sulphobenzylethylpropylsilicyl oxide is decomposed by hot concentrated sodium hydroxide, giving *p*-toluenesulphonic acid.

*33. "**The preparation of conductivity water.**" By **Harold Hartley, Norman Phillips Campbell, and Reginald Holliday Poole.**

The efficiency of different methods of preparing conductivity water has been investigated in order to find a trustworthy way of obtaining water with a specific conductivity not greater than 1 gemmho ($1{\cdot}0 \times 10^{-6}$ reciprocal ohms) in a chemical laboratory under ordinary conditions. By combining several devices in use in other laboratories, a still has been constructed which in one operation gives a fair yield of water with a conductivity 0·75 gemmho at 18°, starting from ordinary distilled water with a conductivity of 5 gemmhos without any preliminary chemical treatment. The distillation can be carried out in a chemical laboratory where nothing is done to keep the air specially free from impurities.

Discussion.

Dr. T. M. Lowry congratulated the authors on being able to produce water of such low conductivity under ordinary laboratory conditions. The still described by Mr. Bousfield (*Trans.*, 1905, **87**, 740) gave almost equally good water (after boiling in a platinum flask, values as low as 0·45 gemmho had been obtained), and had the advantage that it could be left running without attention for a month at a time, but the quality of the water deteriorated when the still was worked in an impure atmosphere, unless special precautions were taken to protect the distillate. It was now generally recognised that the air rather than glass or metal vessels was the most dangerous source of contamination; "gemmho" water could be stored for many months without deterioration in the large green bottles in which the Welsbach solutions were imported, and which could be purchased through the ordinary trade channels; on the other hand, water of lower conductivity did not usually repay the trouble involved in its preparation, since it deteriorated so rapidly in contact with air that it was likely (by giving a false impression of its actual purity) to introduce rather than eliminate an error in conductivity measurements.

Dr. Philip asked whether, in view of the fact that a Jena glass flask was found suitable for storing the pure water, the metal parts of the condenser might not be replaced by Jena glass apparatus.

In answer to Dr. Philip, Mr. Hartley said that very good results had been obtained with a Jena glass condenser, but a block tin tube was better, as it produced more rapid condensation, and could be soldered into the condensing vessel, avoiding the use of corks which required frequent renewal.

***34. "Derivatives of para-diazoiminobenzene." By Gilbert Thomas Morgan and Francis Mary Gore Micklethwait.**

It has been shown that the explosive diazoimino-derivative obtained by Hantzsch from phenyl-*p*-phenylenediamine (*Ber.*, 1902, **35**, 895) belongs to the same group of compounds as the stable arylsulphonyl-*p*-diazoimides prepared by the authors. A series of substances connecting this unstable *p*-diazoimine with the *p*-diazoimides has been obtained by a study of the diazo-derivatives of 2 : 4 : 6-trinitrophenyl-*p*-phenylenediamine, 2 : 4-dinitrophenyl-*p*-phenylenediamine, 4-nitrophenyl-*p*-phenylenediamine, and 2-nitrophenyl-*p*-phenylenediamine.

The first of these bases, which contains a substituent comparable in acidic character to the acyl groups in the arylsulphonyl-*p*-diamines, furnishes a stable *p*-diazoimino-derivative similar in its properties to the arylsulphonyl-*p*-diazoimides, and produced under comparable con-

ditions by the action of sodium acetate on the diazo-salt of 2 : 4 : 6-trinitrophenyl-*p*-phenylenediamine.

The diazo-salts of 2 : 4-dinitrodiphenyl-*p*-phenylenediamine give rise to a diazoimine only when treated with potassium hydrogen carbonate, but not with aqueous sodium acetate. The product is more explosive than the trinitro-derivative.

The diazo-salts of 2- and 4-nitrophenyl-*p*-phenylenediamine do not yield diazoimines either with an alkali acetate or carbonate, but only on treatment with ammonia is the condensation product obtained. In this respect, these bases behave like phenyl-*p*-phenylenediamine itself.

These results show that the ease of formation and the stability of the derivatives of the hypothetical *p*-diazoiminobenzene are determined by the acidic nature of a substituent attached to one aminic nitrogen.

Discussion.

Dr. George Young pointed out that five-atom carbon-nitrogen rings differ markedly in their nature, and especially in regard to their stability, from heterocyclic nuclei containing either a greater or smaller number of atoms in the ring. Hence arguments based on a comparison of the *p*-diazoiminobenzenes with compounds such as *o*-diazoiminobenzene or Wolff's derivative of tetronic acid, which contain five-atom rings, cannot be decisive as between the benzenoid constitution discussed by Dr. Morgan, in which there is a seven-atom and the quinonoid formula with its three-atom heterocyclic grouping.

Dr. Morgan, in reply to Dr. Hewitt, said that in conjunction with Mr. E. G. Couzens he had made many attempts to prepare diazoimides of the meta-series from the benzenesulphonyl-*m*-diamines of benzene, toluene, *m*-xylene, and mesitylene. Being entirely unsuccessful, they inferred that the diazoimide condensation was not wholly a matter of internal salt formation, and that the change occurred only when this factor was reinforced by the tendency for ring formation which characterises the ortho- and para-derivatives as distinguished from the meta-series. The picryl-*p*-phenylenediazoimine closely resembled the para-diazoimides, and it seemed only reasonable to suppose this compound also owed its existence to the combined operation of these salt and ring-forming tendencies.

With regard to the point raised by Dr. Cain in reference to the validity of analogies concerning the constitutions of ortho-, para-, and peri-derivatives based on experimental evidence obtained from the last of these three series, it seemed to him that this testimony was greatly to be preferred to that derived from a comparison instituted between substances so very dissimilar as *p*-aminophenol and α-aminotetronic acid.

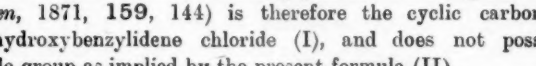
***35. "The affinity constants of bases as determined by the aid of methyl-orange." By Victor Herbert Veley.**

The author has extended the work of which a preliminary account has already appeared (*Proc.*, 1907, **23**, 284).

Results were given for the hydrochlorides of (i) bases not containing an alkyl grouping; (ii) aliphatic amines; (iii) aminoacetic acids, and (iv) uric acid derivatives. As regards hydrazine in (i), and all cases of (iii), it was shown that the results obtained by the methyl-orange method are concordant with those obtained by the electric conductivity method, although the dilutions were about forty to eighty times greater. The tentative conclusion was drawn that either there is a limiting value of V in the Arrhenius equation $K_b/K_w = (1-x)V/x^2$, or that the hydrolytic reaction becomes reversible. As regards cases of (iv), the general agreement of the results obtained by the methyl-orange method with those of the solubility method was considered, although the increase of hydrolysis relative to dilution is less than that required by Arrhenius' formula.

36. "The action of thionyl chloride and of phosphorus pentachloride on the methylene ethers of catechol derivatives." By George Barger.

In the chloro-compounds, formed by heating the methylene ethers of catechol derivatives with phosphorus pentachloride, the most labile chlorine atoms are those introduced into the methylene group. By the action of water or of glacial acetic acid at low temperatures, this pair of chlorine atoms is replaced by an oxygen atom, with the formation of a cyclic carbonate. The "dichlorpiperonal" of Fittig and Remsen (*Annalen*, 1871, **159**, 144) is therefore the cyclic carbonate of 3 : 4-dihydroxybenzylidene chloride (I), and does not possess an aldehyde group as implied by the present formula (II).



(I.) (II.)

Similarly, the supposed chloro-acid, obtained by Fittig and Remsen from piperonylic acid in an impure condition, is in reality the cyclic carbonate of protocatechuoyl chloride or carbonyldioxybenzoyl chloride, $O{:}C{:}O_2{:}C_6H_3{\cdot}COCl$.

Heating with excess of thionyl chloride to 180° has the same effect as phosphorus pentachloride and water, so that cyclic carbonates are formed directly from the methylene ethers.

3 : 4-*Carbonyldioxybenzoyl chloride* boils at 166—167°/12 mm., and crystallises from a mixture of benzene and light petroleum in stout crystals melting at 68°. Several derivatives were described.

37. "A study of the diazo-reaction in the diphenyl series." By Gilbert Thomas Morgan and Francis Mary Gore Micklethwait.

The arylsulphonylbenzidines, $RSO_2\cdot N\overset{*}{H}\cdot C_6H_4\cdot C_6H_4\cdot NH_2$, furnish yellow, crystalline diazonium salts giving rise, on treatment with aqueous sodium acetate, to dark brown, crystalline compounds which are either monohydrated nitrosoamines,

$$R\cdot SO_2\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot NH\cdot NO,H_2O,$$

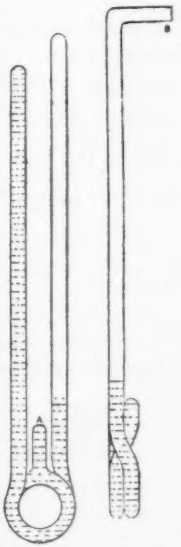
or dihydrated diazoimides (I) :

$$\begin{array}{l} C_6H_4\cdot N_2 \\ | \\ C_6H_4\cdot N\cdot SO_2R,2H_2O \end{array} \qquad \begin{array}{l} C_6H_4\cdot N_2 \\ | \\ C_6H_4\cdot NH \end{array}$$

(I.) (II.)

In this respect, these acylbenzidines differ from benzidine, which gives rise to a diazoimide (II). The diazonium salts of the arylsulphonylalkylbenzidines, $RSO_2\cdot N(C_2H_5)\cdot C_6H_4\cdot C_6H_4\cdot NH_2$, although distinctly less coloured than those of the unalkylated bases, have nevertheless not been obtained in a colourless condition. There is accordingly no reason for supposing that the diazonium salts of the alkylated bases are differently constituted from those which still contain the labile acidic hydrogen atom (*).

38. "A simple manometer for vacuum distillation." By Norman Leslie Gebhard.



The manometer described consists essentially of a barometer tube bent in the form depicted in the figure. The simple trap *A* prevents effectually any air from being forced back into the barometer tube and thus affecting the readings. In order to remove any air thus trapped, it is merely necessary to incline the apparatus so that the mercury expels the air into the open arm again ; this is, however, only necessary at the end of an operation, as the apparatus is capable of yielding accurate readings in spite of the presence of air in the trap.

39. "Researches on the anthraquinones." By William Henry Bentley and Charles Weizmann.

An account was given of the condensations of: (1) phthalic anhydride and pyrogallol trimethyl ether; (2) hemipinic anhydride and veratrole; (3) hemipinic anhydride and pyrogallol trimethyl ether in presence of aluminium chloride. These reactions yield respectively: (1) *trimethoxybenzoylbenzoic acid*, m. p. 169°; (2) *tetramethoxybenzoylbenzoic acid*, m. p. 193—194°; (3) *hydroxytetramethoxybenzoylbenzoic acid*, m. p. 190°. These acids on further condensation with concentrated sulphuric acid yield respectively: (1) *dihydroxymonomethoxyanthraquinone*, m. p. 235—236°; (2) *hydroxytrimethoxyanthraquinone*, m. p. 226°; (3) *trihydroxydimethoxyanthraquinone*, m. p. 230°. By employing phosphoric oxide in place of sulphuric acid, it was found possible to obtain tetramethoxyanthraquinone (m. p. 239°) from tetramethoxybenzoylbenzoic acid.

40. "The formation of 4-pyrone compounds from acetylenic acids." Part. I. By Siegfried Ruhemann.

The author finds that ethyl phenylpropiolate condenses with the ketones of formula $R{\cdot}CH_2{\cdot}CO{\cdot}R'$ in presence of sodium ethoxide to form 4-pyrone derivatives thus:

$$C_6H_5{\cdot}C{\equiv}C{\cdot}CO_2Et + CH_2{\cdot}R{\cdot}CO{\cdot}R' = C_6H_5{\cdot}C\begin{matrix}\langle\\\langle\end{matrix}\begin{matrix}CH{\cdot}CO\\O{-}CR'\end{matrix}\begin{matrix}\rangle\\\rangle\end{matrix}C{\cdot}R + C_2H_6O.$$

Up to the present, acetone and acetophenone have been used, and 2-phenyl-6-methyl-4-pyrone, $C_6H_5{\cdot}C\begin{matrix}\langle\\\langle\end{matrix}\begin{matrix}CH{-}{-}CO\\O{\cdot}C(CH_3)\end{matrix}\begin{matrix}\rangle\\\rangle\end{matrix}CH$, and 2:6-diphenyl-4-pyrone, $C_6H_5{\cdot}C\begin{matrix}\langle\\\langle\end{matrix}\begin{matrix}CH{-}{-}CO\\O{\cdot}C(C_6H_5)\end{matrix}\begin{matrix}\rangle\\\rangle\end{matrix}CH$, respectively, have been obtained.

Along with diphenyl-4-pyrone, there is formed in this reaction a colourless compound, $C_{25}H_{20}O_3$, which yields a violet solution with concentrated sulphuric acid, and is produced according to the equation:

$$C_6H_5{\cdot}C{\equiv}C{\cdot}CO_2Et + 2C_6H_5{\cdot}CO{\cdot}CH_3 = C_{25}H_{20}O_3 + C_2H_6O.$$

The formula $C_6H_5{\cdot}CH_2{\cdot}CO{\cdot}CO{\cdot}C(CO{\cdot}C_6H_5){:}C(CH_3){\cdot}C_6H_5$ is suggested for this substance.

41. "**The action of mustard oils on the ethyl esters of malonic and cyanoacetic acids.**" **By Siegfried Ruhemann.**

Ethyl sodiomalonate reacts with phenyl thiocarbimide, thus: $CHNa(CO_2Et)_2 + C_6H_5\cdot NCS = C_6H_5\cdot N{:}C(SNa)CH(CO_2Et)_2$, and this additive product, with acids, yields diethyl thiocarbanilinomalonate, $C_6H_5\cdot NH\cdot CS\cdot CH(CO_2Et)_2$. This, on hydrolysis with dilute caustic potash, loses 1 molecule of carbon dioxide, forming *thiocarbanilinoacetic acid*, $C_6H_5\cdot NH\cdot CS\cdot CH_2\cdot CO_2H$, which melts at 91—92°, and at the same time evolves carbon dioxide to yield thioacetanilide. The colourless sodium compound of diethyl thiocarbanilinomalonate forms a *benzyl* derivative, which is also colourless, and has the formula $C_6H_5\cdot N{:}C(S\cdot CH_2\cdot C_6H_5)\cdot CH(CO_2Et)_2$.

Ethyl sodiobenzylmalonate and phenyl thiocarbimide do not yield a compound of formula $C_6H_5\cdot N{:}C(SH)\cdot C(CH_2\cdot C_6H_5)(CO_2Et)_2$. This fact would point to a different way of representing the product of the union between ethyl sodiomalonate and phenyl thiocarbimide, but, for the present, the author adheres to the former view.

Ethyl sodiocyanoacetate also combines with phenyl thiocarbimide, and furnishes *ethyl thiocarbanilinocyanoacetate*,

$$C_6H_5\cdot NH\cdot CS\cdot CH(CN)\cdot CO_2Et.$$

This compound is colourless, as are its *sodium* and *ammonium* salts as well as its *benzyl* derivative,

$$C_6H_5\cdot N{:}C(S\cdot CH_2\cdot C_6H_5)\cdot CH(CN)\cdot CO_2Et,$$

but on drying at 100° or on crystallisation from hot solvents it turns yellow. This behaviour is regarded as pointing to the existence of the substance in two tautomeric forms:

$$C_6H_5\cdot N{:}C(SH)\cdot CH(CN)\cdot CO_2Et$$

and $C_6H_5\cdot NH\cdot CS\cdot CH(CN)\cdot CO_2Et$.

The action of ethyl chloroacetate on the sodium derivatives of diethyl thiocarbanilinomalonate and of ethyl thiocarbanilinocyanoacetate yields the *cyclic* compounds:

$$S\!<\!\begin{matrix}CH_2 \text{———} CO\\ C(:NC_6H_5)\cdot C(CO_2Et)_2\end{matrix} \quad \text{and} \quad S\!<\!\begin{matrix}CH_2 \text{———} CO\\ C(:NC_6H_5)\cdot C(CN)\cdot CO_2Et,\end{matrix}$$

respectively; these are yellow, but, under the influence of potassium hydroxide, change into colourless isomerides. The nature of these transformations is still under examination.

42. "The triazo-group. Part II. Azoimides of propionic ester and of methyl ethyl ketone." By Martin Onslow Forster and Hans Eduard Fierz.

On comparing the behaviour of the α- and β-triazo-derivatives of ethyl propionate towards alkali, it was found that, whilst the first-named resembles triazoacetic ester, ethyl β-triazopropionate rapidly parts with hydrazoic acid.

α-Triazopropionic acid, $CH_3 \cdot CHN_3 \cdot CO_2H$, is a colourless oil, having a rancid odour, and forms crystals which melt at 0°; the *silver* salt, $C_3H_4O_2N_3Ag$, crystallises from hot water in lustrous needles. The *ethyl* ester, $C_5H_9O_2N_3$, prepared from ethyl α-bromopropionate and sodium azide, boils at 46° under 2 mm. pressure, and has sp. gr. 1·065 compared with water at 23°; the *amide*, $C_3H_6ON_4$, crystallises from benzene in rectangular plates, melting at 79°.

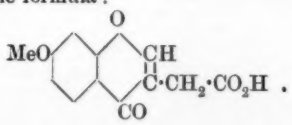
Ethyl-β-triazopropionate, $N_3 \cdot CH_2 \cdot CH_2 \cdot CO_2 \cdot C_2H_5$, prepared from the iodo-ester and sodium azide, boils at 58° under 4 mm. pressure; aqueous ammonia eliminating hydrazoic acid, it has not been possible to prepare the amide and the free acid from this ester.

3-Triazobutanone-2, $CH_3 \cdot CO \cdot CHN_3 \cdot CH_3$, produced on agitating the corresponding chloro-derivative of methyl ethyl ketone with aqueous sodium azide, boils at 46° under 2 mm. pressure, and has sp. gr. 1·057 at 18°; the *semicarbazone*, $C_5H_{10}ON_6$, crystallises in snow-white plates, and melts at 94°.

1-Triazobutanone-2, $N_3 \cdot CH_2 \cdot CO \cdot CH_2 \cdot CH_3$, boils at 56° under 2 mm. pressure, and has sp. gr. 1·084 at 18°; it resembles the foregoing ketone and acetonylazoimide in its behaviour towards alkali and sulphuric acid. The *semicarbazone*, $C_5H_{10}ON_6$, crystallises in needles, and melts at 101°.

43. "Brazilin and hæmatoxylin. Part VIII. Synthesis of brazilinic acid, the lactones of dihydrobrazilinic and dihydrohæmatoxylinic acids, anhydrobrazilic acid, &c. The constitution of brazilin, hæmatoxylin, and their derivatives." By William Henry Perkin, jun., and Robert Robinson.

The authors have continued and elaborated the work of which a preliminary account has already appeared (*Proc.*, 1907, **23**, 291). Further confirmation of the constitution of the members of this group is afforded by the synthesis of *anhydrobrazilic acid*, which has been proved to possess the formula:



ADDITIONS TO THE LIBRARY.

I. *Donations.*

Bruce, *Edwin M.* Detection of the common food adulterants. pp. vii + 84. London 1907 (*Recd.* 5/2/08.)

From the Publishers: Messrs. Archibald Constable and Co.

Cain, *John Cannell.* The chemistry of the diazo-compounds. pp. xi + 172. London 1908. (*Recd.* 6/2/08.) From the Author.

Melick, *Charles W.* Dairy laboratory guide. pp. v + 129. ill. London 1907. (*Recd.* 5/2/08.)

From the Publishers: Messrs. Archibald Constable and Co.

Woburn Experimental Fruit Farm. Eighth report. By the **Duke of Bedford,** *K.G.*, and *Spencer U.* **Pickering.** pp. iv + 129 + xli. London 1908. (*Recd.* 31/1/08.)

From His Grace the Duke of Bedford, K.G.

II. *By Purchase.*

Carlsberg, Laboratoire de. Comptes Rendus. Vol. 6, etc. Copenhague 1903. (*Reference.*)

Lehmann, *O.* Molekularphysik mit besonderer Berücksichtigung mikroskopischer Untersuchungen und Anleitung zu solchen sowie einem Anhang über mikroskopische Analyse. 2 vols. pp. x + 852, vi + 697. ill. Leipzig 1888—1889. (*Recd.* 16/1/08.)

Young, *Sydney.* Stoichiometry. Together with an introduction to the study of physical chemistry by *Sir William* **Ramsay.** pp. lxi + 381. ill. London 1908. (*Recd.* 23/1/08.)

III. *Pamphlets.*

Cain, *John Cannell.* Dyes and dyeing in the past year. A review. (From the *J. Soc. Dyers,* **23,** 1907.)

Richardson, *Clifford.* A plea for the broader education of the chemical engineer. (From the *Proc. Amer. Assoc. Adv. of Sci.*, **57,** 1908.)

At the next Ordinary Meeting on **Thursday,** March **5th**, 1908, at **8.30** p.m., the following paper will be communicated:

"The solubility of iodine in water." By H. Hartley and N. P. Campbell.

R. CLAY AND SONS LTD., BREAD STREET HILL, E.C., AND BUNGAY, SUFFOLK.

Issued 17/3/08

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 24. **No. 338**

Thursday, March 5th, 1908, at 8·30 p.m., Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

Messrs. E. de B. Barnett, E. M. Eagles, R. C. Gale, J. M. Heron, C. W. Moore, A. R. Runeckles, H. E. Watson, and J. H. Williams were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. :

Arthur Edward Coverdale, 68, Broad Street, Worcester.
Frederick J. Maywald, 1028, 72nd Street, Brooklyn, N.Y., U.S.A.
Samuel Ernest Melling, The Cliff, Higher Broughton, Manchester.
Edwin John Watkins, 10, Montpelier Road, Queen's Road, Peckham, S.E.

The PRESIDENT read the names of the Fellows recommended by the Council for election as Officers and as Ordinary Members of Council of the Society. It was also announced that the name of Prof. W. Jackson Pope, as Vice-President, and the names of Mr. John Allan and Prof. Adrian J. Brown, as Ordinary Members of Council, had been proposed by other Fellows.

Of the following papers, those marked * were read :—

***44. "The solubility of iodine in water." By Harold Hartley and Norman Phillips Campbell.**

The solubility of iodine in water has been determined at 18°, 25° 35°, 45°, and 55°, the value at 25° agreeing very closely with that found by Noyes and Seidensticker. The heat of solution has been calculated from the temperature coefficient of the solubility.

***45. "Nitro-derivatives of *o*-xylene." (Preliminary note.) By Arthur William Crossley and Nora Renouf.**

o-Xylene, when treated with a nitrating mixture, readily yields two trinitro-derivatives, which can be separated by means of their different solubilities in concentrated sulphuric acid. Both crystallise from alcohol, in which solvent they are fairly readily soluble, the one in faintly yellow, glistening, flattened needles, melting at 71°, and the other in long, stout, prismatic needles, melting at 115°.

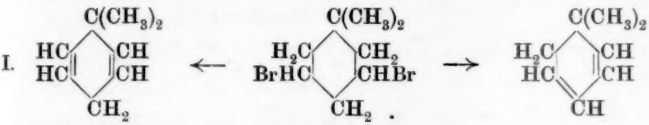
These facts are not in accord with the statement of Noelting and Thesmar (*Ber.*, 1902, **35**, 634), that "*o*-xylene is incapable of yielding a trinitro-derivative even when submitted to the action of the strongest nitrating agents." The explanation of this statement is probably as follows. Noelting and Thesmar further nitrated 4-nitro-*o*-xylene, melting at 29—30°, and obtained two dinitroxylenes, melting respectively at 115—116° and 75—76°. The present authors arrived at the same results on repeating these experiments, except that they have not, so far, been able to raise the melting point of the latter substance above 71°. There are therefore a dinitro- and a trinitro-*o*-xylene, melting at 71°, and also a dinitro- and a trinitro-*o*-xylene melting at 115°. When Noelting and Thesmar submitted 4-nitro-*o*-xylene to the action of a nitrating mixture above a temperature of 100°, they doubtless obtained the two trinitro-derivatives melting at the same temperatures as their dinitro-compounds. The mixed melting-point method, however, shows the substances to be quite distinct; the dinitro- and trinitro-derivatives, melting at 71°, when mixed in equal quantity, melt at 45—50°, becoming quite clear at 63°; and the dinitro- and trinitro-derivatives, melting at 115°, when mixed, melt at 82—83° and become quite clear at 86°.

During the course of these experiments, a third dinitro-*o*-xylene, melting at 82°, has been isolated, and another substance, melting at 115°, which is not a nitroxylene, but a nitro-derivative of some condensed benzene ring derivative.

The authors are continuing the experiments, more particularly in the direction of the orientation of these hitherto unknown nitro-*o*-xylenes.

*46. **"Substituted dihydrobenzenes. Part II. 1 : 1-Dimethyl-$\Delta^{2:4}$-dihydrobenzene and 1 : 1-dimethyl-$\Delta^{2:5}$-dihydrobenzene." By Arthur William Crossley and Nora Renouf.**

Dimethyldihydrobenzene has been prepared by the elimination of two molecules of hydrogen bromide from 3 : 5-dibromo-1 : 1-dimethylhexahydrobenzene, and the resulting hydrocarbon has been



proved to consist of a mixture, in approximately equal parts, of 1 : 1-dimethyl-$\Delta^{2:4}$-dihydrobenzene (II) and 1 : 1-dimethyl-$\Delta^{2:5}$-dihydrobenzene (I). A detailed study of the properties of these substances leads to the conclusion that the 1 : 1-dimethyl-$\Delta^{2:4}$-dihydrobenzene described by Crossley and Le Sueur (Trans., 1902, **81**, 821) has the constitution ascribed to it, despite the adverse criticisms of Harries and Antoni (*Annalen*, 1903, **328**, 88); but it contains traces of some oxygenated substance, probably a methoxy-derivative.

*47. **"The viscosity of aqueous pyridine solutions." By Albert Ernest Dunstan and Ferdinand Bernard Theodore Thole.**

In view of the criticism to which their former work (Trans., 1907, **91**, 1718) has been subjected (Proc., 1908, **24**, 22), the authors have repeated their experiments on the viscosity of aqueous pyridine solutions, and find that the same discontinuities occur in the curve as were previously observed.

DISCUSSION.

Mr. HARTLEY said that he understood Mr. Dunstan to use the word "discontinuity" to denote a point where two supposed sections of a curve pass imperceptibly into one another, but, as under these conditions the curve is continuous, he thought the use of the term "discontinuity" was very misleading. The only evidence for the existence of the secondary irregularities which Messrs. Dunstan and Thole had endeavoured to prove depended on discontinuities in lines

drawn through series of experimental points without making any allowance for experimental error. Such a method of argument was only allowable if around each point a circle was described of radius equal to the probable experimental error. If this were done in the case of the physical properties of mixtures of pyridine and water, he thought that a smooth curve could be drawn through the series of circles so obtained, as had been found by Thomas, Applebey, and himself.

Mr. DUNSTAN agreed with Mr. Hartley as to the difficulty of expressing the change of curvature in a simple way, and thought that perhaps the term "discontinuity" was the simplest in the light of his explanation of the curves. With reference to Mr. Hartley's system of plotting, he was quite in agreement with it, having, as a matter of fact, taken similar precaution in allowing for experimental error.

***48. "The action of thionyl chloride on the methylene ethers of catechol derivatives. II. Piperonyloin, piperil, and hydropiperoin." By George Barger and Arthur James Ewins.**

By heating the methylene ethers, mentioned in the title, with thionyl chloride to 180—200°, cyclic *dicarbonates* result, which in all cases contain chlorine. By elimination of chlorine from the substance derived from piperonyloin and from piperil, the *dicarbonate* of *tetrahydroxybenzil* and *tetrahydroxybenzil*,

$$(OH)_2C_6H_3\cdot CO\cdot CO\cdot C_6H_3(OH)_2,$$

m. p. 237°, was obtained.

A number of other derivatives were described.

49. "Traces of a new tin-group element in thorianite." By Clare de Brereton Evans.

In the course of an examination of some residues of 5 cwt. of thorianite belonging to Sir William Ramsay, traces of a supposed new element were discovered associated with the sulphides of the tin group.

The dark brown sulphide was separated with arsenious sulphide, which it resembles in being insoluble in hydrochloric acid, and readily soluble in ammonium carbonate solution, to which it gives a characteristic deep brown colour. In addition to these reactions, it dissolves readily in water, forming a deep brown solution; it is scarcely attacked by a mixture of hydrochloric acid and potassium chlorate, but dissolves in nitric acid, forming, on evaporation at 100°, a golden-red syrup, which leaves behind a hygroscopic, brown oxide at

120—130°. A grey metal was obtained by reduction in hydrogen, but the quantity was too small to allow of its equivalent being determined.

Incidentally, proof was obtained of the presence in thorianite of arsenic, mercury, bismuth, molybdenum, and selenium, in addition to those elements already discovered in the mineral.

A new triple oxalate of thorium, uranium, and ammonium was described; it appears to have the composition

$$ThU_25(NH_4)_2(C_2O_4)_{10},14H_2O.$$

50. "**The sulphination of phenolic ethers and the influence of substituents.**" **By Samuel Smiles and Robert Le Rossignol.**

The authors have previously drawn the conclusion (Proc., 1906, **22**, 158; Trans., 1906, **89**, 696) that the sulphonium base derived from phenetole is produced in three stages at which the sulphinic acid, sulphoxide, and base are consecutively formed. The sulphinic acid, however, had not been observed in the products of the reaction, and thus the evidence was incomplete. The above view of the mechanism of the reaction has now been confirmed by the isolation of the sulphinic acid from substituted phenolic ethers. It is proposed to apply to the entire process the name "sulphination." The behaviour of benzene, toluene, and homologous phenolic ethers has been investigated, and it was shown that the products vary according to the position of the methoxyl and methyl groups. Generally speaking, the presence of a group in the ortho-position with respect to the entrant quadrivalent sulphur atom tends to prevent the formation of sulphonium base; on the other hand, this is favoured by groups of strong directing influence.

51. "**The relation between unsaturation and optical activity. Part. II. Alkaloid salts of corresponding saturated or unsaturated acids.**" **By Thomas Percy Hilditch.**

The study of the relative effects of saturated and unsaturated acids on an optically active base has been extended to alkaloid salts of β-phenylpropionic, cinnamic, phenylpropiolic, and succinic, maleic, fumaric, and acetylenedicarboxylic acids. Salts of brucine, coniine, codeine, and cinchonine have thus been examined polarimetrically in chloroform solution, and the results show very clearly that the change in optical rotatory power is influenced not only by the simple change of constitution associated with increasing unsaturation, but also by the structure of the base and the type of acid used. Thus, in general, the

effect observed in the case of coniine salts differs from those observed with the derivatives of more complex bases, and appears to be of the same kind as that observed by Walden with the active amyl esters of the same series of acids. It is noticeable, however, that in all the instances now brought forward the change to an ethylenic linking is accompanied by an increase in optical effect.

52. "The wandering of bromine in the transformation of nitroaminobromobenzenes." By Kennedy Joseph Previté Orton and Constance Pearson.

2 : 6-Dibromo-1-nitroaminobenzene, when dissolved in aqueous, aqueous alcoholic, or acetic acid solutions of hydrochloric or sulphuric acids, yields not only 2 : 6-dibromo-4-nitroaniline, but also the isomeric 2 : 4-dibromo-6-nitroaniline, the nitro-group having partly migrated to the vacant para-position, and having partly displaced an atom of bromine from one of the ortho-positions.

The use of hydrobromic or nitric acid in the same solvents leads largely to the reduction of the nitroamine to the diazo-compound, but at the same time migration of the nitro-group and displacement of bromine occur.

In a comparison, the behaviour of other nitroamines when similarly treated was described.

53. "A new isomeride of vanillin occurring in the root of a species of Chlorocodon." (Preliminary note.) By Ernest Goulding and Russell George Pelly.

A sample of the root of a species of *Chlorocodon* (probably *C. Whiteii*) was forwarded for examination to the Imperial Institute from Uganda, where the plant is known by the native name of "Murundo." This root has a pleasant odour, intermediate between those of vanillin and piperonal, and is said to be chewed by the natives for sweetening the breath.

The powdered root, on distillation with steam, yields 0·5 per cent. of a crystalline *substance*, $C_7H_5O_2{\cdot}OMe$, which separates from the distillate in thin, lustrous, colourless plates, having the characteristic odour of the root. It melts at 41—42° and boils at 257—258°, a pale brown coloration being developed. The substance is readily soluble in most organic solvents, and fairly so in hot, but only sparingly so in cold, water. An aqueous solution gives a red or purplish-brown coloration with ferric chloride, and, on warming a solution with ammoniacal silver nitrate, the latter undergoes

reduction with the separation of silver. It dissolves freely in dilute alkali hydroxide, and is reprecipitated by acids. The aqueous solution does not give a precipitate with lead acetate.

The *oxime*, $OMe{\cdot}C_6H_3(OH){\cdot}CH{:}N{\cdot}OH$, crystallises in large, thin, lustrous, transparent plates, melting at 138°; it is almost odourless, and readily soluble in hot water but sparingly so in cold.

The *phenylhydrazone*, $OMe{\cdot}C_6H_3(OH){\cdot}CH{:}N{\cdot}NHPh$, crystallises from hot alcohol in pale yellow, lustrous plates, and melts at 137—138°.

The *sodium* derivative, $OMe{\cdot}C_6H_3(CHO){\cdot}ONa$, obtained by the addition of alcoholic sodium hydroxide to an alcoholic solution of the substance, separates in small, almost colourless, lustrous plates, and dissolves readily in water to form a pale yellow solution which is strongly alkaline.

These results, together with the analytical data obtained, show that the odorous constituent of *Chlorocodon* root is a monomethyl ether of a dihydroxybenzaldehyde, $OMe{\cdot}C_6H_3(OH){\cdot}CHO$, which is not identical with vanillin or any of its known isomerides.

Unfortunately, the amount of material available was so small that it has not been possible to carry out experiments with the object of ascertaining the relative positions of the hydroxy-, methoxy-, and aldehyde-groups, but the authors intend to continue the work in this direction as soon as a further supply of the root has been obtained.

54. "The volatile oil of the leaves of Ocimum viride." (Preliminary note). By Ernest Goulding and Russell George Pelly.

A consignment of the leaves of *Ocimum viride*, forwarded for examination to the Imperial Institute from Sierra Leone, has been examined with the following results. On distillation with steam, the leaves yielded about 0·35 per cent. of an orange-yellow, volatile oil, which is very mobile, has an aromatic, thyme-like odour, a spicy, pungent taste, D_{15}^{15} 0·9115, $[\alpha]_D + 1°30'$ (approx.), and is soluble in all proportions in 90 per cent. alcohol.

When distilled under the ordinary pressure, 100 c.c. of the oil yielded 25 c.c. boiling at 165—180°, with D_{15}^{15} 0·8614 and $[\alpha]_D + 0°33'$; 20 c.c. at 180—200°, with D_{15}^{15} 0·8804 and $[\alpha]_D + 1°40'$; 20 c.c. at 200—220°, with D_{15}^{15} 0·9164 and $[\alpha]_D + 2°38'$; 20 c.c. at 220—235°, with D_{15}^{15} 0·9548 and $[\alpha]_D + 3°38'$; and 10 c.c. at 235—250°, with D_{15}^{15} 0·9565 and $[\alpha]_D + 5°14'$.

The composition of the oil is approximately as follows: thymol, 32 per cent.; alcohols (calculated as $C_{10}H_{18}O$), 40 per cent.; esters

(calculated as $C_{10}H_{17}\cdot OAc$), 2 per cent.; the remainder consists chiefly of a terpene (or possibly a mixture of terpenes), $C_{10}H_{16}$, which is a mobile, highly refractive liquid of pleasant, lemon-like odour, boiling at 160—166°, and having D_{15}^{15} 0·8456 and $[\alpha]_D + 0°10'$.

The authors intend to make a more complete examination of the oil as soon as a larger supply of material has been received.

55. "Experiments on the synthesis of the terpenes. Part XII. Synthesis of terpins, terpineols, and terpenes derived from the methyl*iso*propyl*cyclo*pentanes, $Me\cdot C_5H_8\cdot CHMe_2$." By Walter Norman Haworth and William Henry Perkin, jun.

An account was given of the synthesis of terpenes, such as

$$CH\begin{<}\begin{matrix}CH\cdot CH_2\\ CHMe\end{matrix}\end{>}CH\cdot CMe{:}CH_2,$$

which are analogously constituted to dipentene, but contain a *cyclo*pentene in the place of the *cyclo*hexene ring of the latter. The corresponding five-ring terpineols and terpins were also described.

56. "The initial change of the radium emanation." By Nevil Vincent Sidgwick and Henry Thomas Tizard.

In their paper on this subject, Cameron and Ramsay (*Trans.*, 1907, **91**, 1266) have shown that, after the removal of the hydrogen and oxygen, the radium emanation diminishes rapidly (in about an hour and a-half) to one-half of its initial volume. Hence it follows that the emanation (or a constituent) polymerises; the possibility of the simultaneous formation of helium or of a solid they consider they have disproved.

By measuring the rate of change, they show that the reaction is unimolecular, that is, the rate is proportional only to the amount of changing substance. They assume that two molecules of the original emanation Em_1 polymerise to one molecule of Em_2, and they say (p. 1280) "This involves an exponential curve, and that has been realised." But their exponential curve implies a unimolecular reaction, and a polymerisation cannot in the nature of things be unimolecular, since it necessarily involves the combination of two or more molecules. The reaction:

$$2Em_1 = Em_2$$

must be bimolecular, and, in general, any polymerisation must be a reaction of the n^{th} order, where n is the number of molecules that combine.

Hence the change they are measuring cannot be the polymerisation, and, as it is unimolecular, must be of the form :

$$\mathrm{Em}_1 = \mathrm{Em}',$$

and the polymerisation which obviously occurs must follow this change and must be rapid. We therefore have :

(1) $\mathrm{Em}_1 = \mathrm{Em}'$ (Slow : unimolecular)

(2) $n\mathrm{Em}' = \mathrm{Em}_2$ (Quick : n-molecular).

Cameron and Ramsay assume that $n = 2$: that two molecules of Em_1 give one of the final product. But this is not a necessary result of their equation, for, if the first reaction is unimolecular, we get :

$$-\frac{dV'_t}{dt} = kV't,$$

where V'_t is the amount af the changing substance Em_1 (or its volume reduced to standard pressure) at the time t from the true beginning of the reaction, the observed volume of gas being V_t. Now if n molecules of the first product (Em') polymerise to one molecule of Em_2, the amount of Em_2 present at time t is obviously :

$$(V_o - V_t)\frac{1}{n-1},$$

where V_o is the total volume of gas at the beginning.

Therefore
$$V'_t = V_t - (V_o - V_t)\frac{1}{n-1}$$
$$= \frac{nV_t - V_o}{n-1}$$
$$= \frac{n(V_t - V_\infty)}{n-1},$$

since V_∞, the final volume, $= V_o/n$.

Hence
$$-\frac{dV'_t}{dt} = \frac{n}{n-1} \cdot \frac{dV_t}{dt} = kV'_t$$
$$= \frac{n}{n-1} \cdot k \cdot (V_t - V_\infty).$$

Therefore
$$-\frac{dV_t}{dt} = k(V_t - V_\infty).$$

Integrating this, under the condition that when $t = 0$, $V_t = V_o$, we obtain
$$\log\frac{V_o - V_\infty}{V_t - V_\infty} = kt,$$

which is the expression that Cameron and Ramsay have shown to

agree with the experimental results. It is obvious that it is equally compatible with any value of n.

Their reason for assuming that $n=2$ is that during the time of observation the volume of the gas diminishes to about a half; and they suppose that the time when the first observation is made is the actual beginning of the change, and that the gas then wholly consists of Em_1. It is, however, difficult to see how the reaction cannot have begun earlier than this. The emanation gradually accumulates in and over the solution of the radium salt for several days; it is then transferred to the explosion-burette, exploded, the emanation and the residual hydrogen passed over phosphoric oxide and cooled with liquid air, the hydrogen pumped off, and the emanation allowed to evaporate and passed into the capillary. Mr. Cameron informs us that the time taken in the purification is less than an hour, and the time elapsing between the evaporation of the emanation and the first measurement is less than a quarter of an hour. It seems scarcely possible that the change of Em_1 to Em′, which, as it is unimolecular, is not affected by the dilution, should not take place during these operations, and yet when they are finished should begin with a velocity which takes it to half completion in about nine minutes. A more probable hypothesis is that the change has already proceeded some way before the observations begin, and that the actual number of molecules of Em_1 which go to form one molecule of Em_2 is greater than 2. Even if the reaction only begins when the liquid air has been removed, and the gas has assumed the temperature of the room, something like half the initial volume of Em_1 must have changed before the first measurement is made. On the other hand, the change cannot have continued during the whole time that the emanation has been accumulating, for, if we reckon the time backwards, the volume must increase a thousandfold every ninety minutes. It would therefore appear that for some reason the reaction does not begin until the liquid air is removed; before this point, the Em_1 must have been in a different chemical state. But as soon as the emanation has evaporated, it must begin to change at once, and, as it is not measured for nearly ten minutes after this, the volume of Em_1 at the first measurement cannot be much more than half the true initial volume, the period of half decay being about nine minutes. Hence the final volume is at most one-third of the initial, and n cannot be less than 3.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Dyer, *Bernard.* Fertilisers and feeding stuffs. Their properties and uses. With the full text of the Fertilisers and Feeding Stuffs Act, 1906, the regulations and forms of the Board of Agriculture, and notes on the Act by *A. J.* **David.** 5th edition. pp. viii + 150. London 1908. (*Recd.* 22/2/08.) From the Author.

Geological Society of London. The history of the Geological Society of London. By *Horace B.* **Woodward.** pp. xx + 336. ill. London 1907. (*Recd.* 20/2/08.) From the Society.

Glasgow, University of. Register of Members of the General Council . . . for the year commencing 1st January, 1908. pp. 163. Glasgow 1907. (*Recd.* 26/2/08.) From the University.

Menschutkin, *Boris N.* Life and work of N. A. Menschutkin. pp. viii + 376. ill. 1908. [In Russian.] (*Recd.* 11/1/08.) From the Author.

Rawson, *Christopher.* Report on the cultivation and manufacture of Indigo. (*For the Behar Indigo Planters' Association, Limited.*) 2nd edition. pp. 97. Calcutta 1907. (*Recd.* 25/2/08.) From the Author.

Society of Public Analysts. General index to "**The Analyst.**" Vols. xxi—xxx., 1896—1905. Compiled by *J. Cuthbert* **Welch.** pp. 352. London 1906. (*Reference.*) From the Society.

II. *By Purchase.*

Arrhenius, *Svante.* Untersuchungen über die galvanische Leitfähigkeit der Elektrolyte. Translated by *Anna* **Hamburger** and edited by *Otto* **Sackur.** (Ostwald's *Klassiker,* No. 160.) pp. 153. ill. Leipzig 1907. (*Recd.* 27/2/08.)

Cohen, *Ernst.* Das Lachgas. Eine chemisch-kultur-historische Studie. pp. vi + 99. ill. Leipzig 1907. (*Recd.* 19/2/08.)

Francis, *Francis,* and **Fortescue-Brickdale,** *J. M.* The chemical basis of pharmacology. An introduction to pharmacodynamics based on the study of the carbon compounds. pp. xii + 372. London 1908. (*Recd.* 19/2/08.)

Fraunhofer, *Joseph.* Bestimmung des Brechungs- und Farbenzerstreuungs-Vermögens verschiedener Glasarten in bezug auf die Vervollkommnung achromatischer Fernröhre. Edited by *Arthur von* **Oettingen.** (Ostwald's *Klassiker,* No. 150.) pp. 36. ill. Leipzig 1905. (*Recd.* 27/2/08.)

ANNUAL GENERAL MEETING.

The Annual General Meeting of the Society for the election of Officers and Council, and other business, will be held on Thursday, March 26th, 1908, at five o'clock in the afternoon.

The President will deliver his address, entitled: "The Electron as an Element."

LOTHAR MEYER MEMORIAL.

The Council has decided to make a donation of £10 to the Lothar Meyer Memorial Fund.

Many old pupils and admirers of the author of "Die Modernem Theorien der Chemie" may be desirous of contributing to this Memorial, and the Treasurer will be glad to receive, at an early date, subscriptions from Fellows and others to the Fund.

Cheques, &c., should be made payable to Dr. Alexander Scott, crossed "Lothar Meyer Memorial Fund A/c.," and sent to the Treasurer, Chemical Society, Burlington House, W.

ERRATA.

1908. P. 48, line 13 from below, and p. 51, line 5 from top, *for* "**Francis**" *read* "**Frances.**"

At the next Ordinary Meeting on **Thursday**, March **19th**, 1908, at **8.30** p.m., the following papers will be communicated:

"The constitution of electronegative 'thiocyanates.'" By A. E. Dixon and J. Taylor.

"An improved form of pyknometer." By W. R. Bousfield.

"The quantitative conversion of aromatic hydrazines into diazonium salts." By F. D. Chattaway.

"The action of heat on α-hydroxycarboxylic acids. Part IV. Racemic αα-dihydroxyadipic acid and meso-αα-dihydroxyadipic acid." By H. R. Le Sueur.

"The spontaneous crystallisation of sodium sulphate solutions." By H. Hartley, B. M. Jones, and G. A. Hutchinson.

"Quantitative relations of salts of thallium, and its separation from silver." By J. F. Spencer and Miss M. Le Pla.

"Constitution of hydroxyazo-compounds. Action of diazomethane and of mercuric acetate." By C. Smith and A. D. Mitchell.

RICHARD CLAY AND SONS, LTD., BREAD STREET HILL, E.C. AND BUNGAY, SUFFOLK.

Issued 30/3/08

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 24. **No. 339**

Thursday, March 19th, 1908, at 8.30 p.m., Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

Messrs. W. R. Bousfield, M. J. A. Braun, J. A. Carpenter, T. P. Hilditch, O. Oberländer, A. W. Oke, and T. M. Tyson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs.:

Leonard Clifford Green, B.E., Wienholt St., Torwood, Brisbane.
William Hall, B.Sc., Inglewhite, Manchester Road, Bolton.
Hugo Stefan Kohn, Ph.D., 3A, Hythe Road, Willesden Junction.
Gerald Roche Lynch, 160, Holland Park Avenue, W.

The PRESIDENT announced that Professor W. Jackson Pope had expressed himself unwilling to accept nomination for Vice-Presidency.

Of the following papers, those marked * were read:—

***57. "A new form of pyknometer." By William Robert Bousfield.**

The author described a new form of pyknometer, intended for very accurate density determinations.

***58. "The action of heat on α-hydroxycarboxylic acids. Part IV. Racemic αα′-dihydroxyadipic acid and meso-αα′-dihydroxyadipic acid." By Henry Rondel Le Sueur.**

When αα′-dihydroxyadipic acid melting at 146° (compare *Proc.*, 1907, **23**, 196) is heated above its melting point, it loses water, and its dilactone (m. p. 134°) is formed as a crystalline sublimate. The acid has been resolved into its optical antipodes by fractional crystallisation of its cinchonidine salt. The *d*-acid melts at 157°, and has $[\alpha]_D^{16} + 3{\cdot}8°$; its *ammonium* salt is lævorotatory and has $[\alpha]_D^{11} - 21{\cdot}4°$..

When the αα′-dihydroxyadipic acid melting at 174° is heated at 180—190°, it loses water, forming a lactone-lactide. All attempts to resolve this acid have failed, and it must therefore be regarded as the meso- or internally compensated variety.

That the acid which admits of resolution into its optically active components readily forms a dilactone, whereas the meso-variety does not, is in complete agreement with the spacial formulæ of these substances. Characteristic derivatives of both acids have been prepared.

***59. "The spontaneous crystallisation of sodium sulphate solutions." By Harold Hartley, Bernard Mouat Jones, and George Adrian Hutchinson.**

The authors have examined the spontaneous crystallisation of sodium sulphate solutions, and have found that if the solutions are subjected to mechanical friction three of the four possible solid phases, namely, ice, $Na_2SO_4,7H_2O$ and Na_2SO_4, are produced spontaneously at definite temperatures. Supersolubility curves have been traced for these three phases which, in conjunction with the solubility curve, define the labile and metastable regions for the system. The spontaneous crystallisation of the fourth solid phase, $Na_2SO_4,10H_2O$, is of rare occurrence compared with that of $Na_2SO_4,7H_2O$, and seems to take place irregularly without any definite relation to the temperature and concentration of the solution.

***60. "Constitution of hydroxyazo-compounds. Action of diazomethane and of mercuric acetate." By Clarence Smith [and, in part, Alec Duncan Mitchell].**

Diazomethane reacts with *p*-hydroxyazo-compounds to form the methyl ethers obtained by the ordinary methods of alkylation.

Benzeneazo-*p*-cresol, *p*-chlorobenzeneazo-*p*-cresol, and β-benzeneazo-α-naphthol do not react with diazomethane.

The action of mercuric acetate in boiling aqueous-alcoholic solution on benzeneazophenol, 2 : 4 : 6-tribromobenzeneazophenol, benzeneazo-*o*-nitrophenol, benzeneazo-*oo'*-dibromophenol, benzeneazo-*p*-cresol, and benzeneazo-*o*-bromo-*p*-cresol has been examined, with the result that the number of mercuriacetate groups entering the molecule of the hydroxyazo-compound is equal to the number of unsubstituted positions in the ortho-position with respect to the oxygen atom. The substances obtained are yellow, red, or reddish-brown compounds, readily soluble only in acetic acid, and not melting below 300°, with the exception of benzeneazo-*p*-cresol mercuriacetate,

$$C_6H_5 \cdot N_2 \cdot C_7H_5(OH) \cdot Hg \cdot CO_2 \cdot CH_3,$$

which melts at 269—270° with decomposition, and is identical with the compound obtained by Dimroth (*Ber.*, 1902, **35**, 2864). The corresponding mercurichlorides and mercuribromides have been obtained from the mercuriacetates by means of sodium chloride or potassium bromide in alkaline or acetic acid solution.

Discussion.

Mr. Baly wished to put in a plea for the spectroscopic evidence which so decidedly pointed to the fact that, of the hydroxyazo-compounds, the ortho were quinonehydrazones, whilst the para had the true hydroxyazo-structure. He emphasised the fact that where a possibility of tautomerism existed as in the case under discussion, chemical means failed to determine which of the two possible desmotropic forms a substance possessed. Mr. Tuck had shown that the quinonehydrazone form, on the one hand, and the hydroxyazo-form, on the other, each represented by compounds the structure of which was beyond cavil, exhibited two types of spectra which differed very greatly in the relative dilution at which the absorption bands appeared, and also in the shape of the bands themselves. Inasmuch as the parent hydroxyazo-compounds conformed to one or other of these types, so was their constitution in alcoholic solution established notwithstanding any chemical evidence to the contrary.

It appeared further from Dr. Smith's paper that a slightly different interpretation might be put upon his results. Dr. Smith had pointed out that, in the case of the para-hydroxyazo-compounds, both methyl sulphate and diazomethane introduce a methyl group into the hydroxyl group, thus proving the hydroxyazo-configuration. In the case of the ortho-compound, diazomethane had no action and methyl sulphate only acted at 100°, and then the compounds behaved as if they possessed the hydroxyazo-structure. Again, Dr. Smith had pointed out that

his experiments with mercuric acetate were carried out at 85°, but he (the speaker) thought these results rather led one to believe that the para-hydroxyazo-compounds were true hydroxyazo-bodies, but that the ortho-isomerides were quinonehydrazones at the ordinary temperature, and at 100° they tended to favour the hydroxyazo-form. In other words, as the temperature rose the equilibrium between quinonehydrazone and hydroxyazo-forms was shifted towards the hydroxyazo-side, so that at 100° the compounds could react in this form.

Dr. MORGAN said that, in 1889, Professor Meldola and he had found that benzeneazo-β-naphthol could be benzoylated and ethylated only with some difficulty, and that the products, when mildly reduced in the presence of acids, underwent the benzidine transformation to 4 : 4′-diaminophenylnaphthyl bases which still contained the benzoyl and ethyl groups attached to the phenolic oxygen. They drew from these results the conclusion that the acyl and alkyl derivatives of benzeneazo-β-naphthol were true azo-compounds and not β-naphthaquinonehydrazones. It was interesting to find that the authors held the view that the ortho-hydroxyazo-compounds were really azo- and not hydrazino-derivatives.

The presence of many other constituents, besides the azo-group, in the contiguous α-position greatly modified the properties of β-naphthol or β-naphthylamine, but it was scarcely possible in every instance to ascribe this effect to the existence of a quinonoid configuration.

Dr. HEWITT drew attention to the fact that benzeneazo-*p*-cresol behaved as a phenol towards substituting agents even at the ordinary temperature. A cold solution of the substance in glacial acetic acid, containing excess of fused sodium acetate, brominated exclusively in the phenolic nucleus.

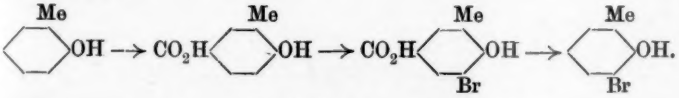
It should be remembered that spectrographic evidence, valuable though it was, ultimately depended on the determination of the constitution of typical substances by chemical methods.

Dr. SMITH, in reply, expressed the opinion that the spectrometric evidence by no means conclusively proved the quinonehydrazone structure of *o*-hydroxyazo-compounds and of their acyl derivatives. Benzoquinonebenzoylphenylhydrazone, which was undoubtedly a quinonehydrazone, gave a totally different absorption spectrum from that of the isomeric benzoylbenzeneazophenol, which had the azo-structure, whilst benzoylbenzeneazo-*p*-cresol gave an absorption curve closely resembling that of benzeneazophenol. With regard to the point raised by Mr. Tuck, the reduction of β-benzeneazo-α-naphthyl acetate resulted first in the formation of the hydrazo-compound, then wandering of the acyl group from the oxygen to either of the nitrogen atoms

took place, and, finally, fission occurred, yielding the four products, aniline and *N*-acetyl-2-amino-1-naphthol, acetanilide and 2-amino-1-naphthol.

***61. "Orthobromophenols and some bromonitrophenols." By Philip Wilfred Robertson.**

The method of direct bromination cannot be employed for the preparation of *o*-bromo-*o*-cresol or the corresponding *o*-bromoguaiacol. Accordingly, these compounds were obtained by an indirect method as is indicated in the following scheme, illustrating the changes in the case of *o*-cresol:



The constitution of the *o*-bromo-derivatives was confirmed by the fact that on nitration they yielded the same *o*-bromo-*p*-nitrophenols as are obtained from the *p*-nitrophenols by bromination.

o-*Bromo*-p-*nitro*-o-*cresol*, p-*bromo*-o-*nitro*-o-*cresol*, and o-*bromo*-p-*nitro*-*guaiacol* form a red and a yellow series of *potassium* salts, being a confirmation of the recent work of Hantzsch (*Ber.*, 1907, **40**, 330).

Bromonitrothymol is anomalous, as only one isomeride (m. p. 109°) is obtained by the reactions: (1) nitration of *p*-bromothymol, (2) bromination of *o*-nitrothymol, (3) nitration of *o*-bromothymol, (4) bromination of *p*-nitrothymol; this isomeride must be o-*bromo*-p-*nitrothymol*, as it forms bromo-*p*-thymoquinone on oxidation.

62. "The constitution of thiocyanates containing an electronegative group." By Augustus Edward Dixon and John Taylor.

Examination of a number of acylthiocarbimides shows the contained ·NCS group to have the same refraction value as in hydrocarbon thiocarbimides; since this holds also for acetyl "thiocyanate" (Hawthorne, *Trans.*, 1906, **89**, 556), it seems probable that the ·NCS group is contained equally in acyl "thiocyanates" and acylthiocarbimides, true acyl thiocyanates being still unknown.

Moreover, the partial decomposition with formation of thiocyanic acid characteristic of "acyl thiocyanates" also takes place in the case of acylthiocarbimides, the latter undergoing this change with caustic alkalis or alkaline bases, but not with arylamines. The chemical differences between acyl thiocyanates and acylthiocarbimides

are due, not to diversity of constitution, but to the variable resistance offered by the acyl radicle to its separation from the combined ·NCS group; when this is high, thiocarbimidic function preponderates, and when low, thiocyanic decomposition. Hence external circumstances, in so far as they affect that separation, may predominate in determining the direction of change.

Diphenylamine unites with acetyl, benzoyl, carboxymethyl- or carboxyethyl-thiocarbimide, forming an *a*-acyl-*bb*-diphenylthiocarbamide. a-*Acetyl*-bb-*diphenylthiocarbamide*, m. p. 141° (corr.), gives with alcoholic potash aa-*diphenylthiocarbamide*, m. p. 212°, and by distillation yields acetylthiocarbimide, identical with the compound produced from acetyl chloride and metallic thiocyanates; with acetic anhydride, *aa*-diphenylthiocarbamide regenerates *a*-acetyl-*bb*-diphenyl thiocarbamide.

a-*Benzoyl*-bb-*diphenylthiocarbamide*, a-*carboxymethyl*-bb-*diphenylthiocarbamide*, and a-*carboxyethyl*-bb-*diphenylthiocarbamide* melt at 135°, 128°, and 125° respectively; by lead or silver salts these trisubstitution compounds are desulphurised with difficulty, or not at all.

a-*Carboxymethyl*-ab-*diphenylthiocarbamide*, isomeric with the *bb*-diphenyl derivative, is obtained from methyl chlorocarbonate and thiocarbanilide; it melts at 106°, and, like *a*-carboxyethyl-*ab*-diphenylthiocarbamide, is desulphurised readily by alkaline salts of silver or lead.

63. "The quantitative conversion of aromatic hydr. . .to diazonium salts." By Frederick Daniel Chattaway.

All primary aromatic hydrazines can be quantitatively converted into the corresponding diazonium salts either by chlorine or by bromine.

If either halogen be allowed to act at a low temperature on the hydrazine dissolved in alcohol, the diazonium salt separates out in a pure state.

Unless, however, the solid salt is required, the operation can be most easily carried out by dissolving the hydrazine in glacial acetic acid, cooling the solution to about −15° by the addition of crushed ice, and either passing in a rapid stream of chlorine or adding the calculated quantity of bromine dissolved in acetic acid and similarly cooled by ice.

The formation of the diazonium salt is without doubt effected by a substitution of two atoms of hydrogen in the hydrazino-group by halogen, followed by the elimination of halogen acid, thus:

$$\begin{array}{l} C_6H_5\cdot N\cdot H \\ \quad\quad | \\ H\cdot N\cdot H \end{array} \longrightarrow \begin{array}{l} C_6H_5\cdot N\cdot Cl \\ \quad\quad | \\ H\cdot N\cdot Cl \end{array} \longrightarrow \begin{array}{l} C_6H_5\cdot N\cdot Cl \\ \quad\quad \| \\ \quad\quad N \end{array}$$

As in other cases where hydrogen attached to nitrogen is replaced by halogen, an additive product is probably first formed, in this instance by the addition of four halogen atoms, each nitrogen atom becoming quinquevalent, the elimination of halogen acid then gives rise to the diazonium salt, which being stable under the conditions of the experiment can be isolated.

64. "Quantitative separation of thallium from silver." By James Frederick Spencer and Margaret Le Pla.

A quantitative separation of the salts of silver and thallium is effected by treating the mixture with a stream of chlorine, whereby the thallium is oxidised to the very soluble thallic chloride and the silver is precipitated as silver chloride. After removing the latter, the solution is concentrated, and reduced by means of sulphur dioxide (either liquid or gaseous). The excess of sulphur dioxide is removed by boiling, and the thallium precipitated as thallous iodide, filtered, washed, and dried at 140°. The results are quantitative, and are obtained very quickly.

Thallous chloride was found to be more soluble in potassium carbonate than in water, for whereas water dissolves 3·86 grams per litre at 25°, a 5*N*-solution of potassium carbonate dissolves 21·84 grams per litre at the same temperature.

65. "Molecular volumes of the nitrites of silver, mercury, and the alkali metals." By Prafulla Chandra Rây.

The author finds that the molecular volumes of the nitrites of lithium, sodium, potassium, silver, and mercury are 63·44, 63·98, 88·88, 69·16, and 83·04 respectively.

66. "Lithium nitrite and its decomposition by heat." By Prafulla Chandra Rây.

Lithium nitrite is a mono-hydrated salt, and does not crystallise with half a molecule of water as stated by Lang.

In its general properties it resembles the nitrites of the other alkali metals.

67. "The existence in aqueous solutions of a univalent cadmium ion, a subvalent thallium ion, and a bivalent bismuth ion." By Henry George Denham.

The method of continuous circulation used by Denham and Allmand (*Trans.*, 1908, **93**, 424) to prove the existence of a univalent lead ion in aqueous solution has been applied to investigate the existence of similar ions of other metals.

A hot solution of cadmium sulphate was kept circulating over a column of granulated cadmium, and in thirty-six hours well-marked crystals began to appear, proving that the ionic reaction $Cd^{\cdot\cdot} + Cd \longrightarrow 2Cd^{\cdot}$ had taken place with absorption of heat, and had been reversed in the cold part of the apparatus.

Granulated thallium, in contact with a solution of thallous sulphate, gave a similar crystalline deposit in three days, demonstrating the reaction $Tl^{\cdot} + Tl \longrightarrow Tl_2^{\cdot}$, and in the light of this experiment it is considered probable that the darkening of thallous haloid salts on exposure to sunlight is due to the formation of coloured sub-haloid salts, analogous to the case of silver.

Bismuth, heated in contact with a solution of the oxychloride in hydrochloric acid, soon gave unmistakable evidence of the production of the ion $Bi^{\cdot\cdot\cdot}$, but it is of interest that no evidence for such an ion was obtained in the case of arsenic or antimony. Nickel and nickel sulphate solution showed no signs of crystals, although in this case a suboxide Ni_2O has been described.

68. "Note on the oxidation of phenylhydrazine by Caro's acid." By John Cannell Cain.

In explaining the mechanism of the oxidation of aromatic hydrazines by free oxygen and other oxidising agents, Chattaway (*Trans.*, 1907, **91**, 1323; 1908, **93**, 270) assumes the formation of an unstable hydroxyhydrazine which immediately loses water and nitrogen, thus:

$$\begin{matrix} R & H \\ \dot{N}—\dot{N} \\ \dot{H} & \dot{O}H \end{matrix} \longrightarrow \begin{matrix} R\cdot H \\ N_2 \\ H\cdot O\cdot H \end{matrix} .$$

The presence of such a hydroxyhydrazine was not observed by Chattaway, as the oxidation always proceeded with immediate evolution of nitrogen, but striking confirmation of this hypothesis is afforded when phenylhydrazine (1 mol.) is oxidised by Caro's acid (equivalent to 1 atom of oxygen). When ice-cold, neutral, aqueous

solutions (saturated with ether) of these agents are mixed together, a greenish-yellow coloration is immediately produced; this persists for some seconds, when vigorous evolution of nitrogen begins, the greenish-yellow coloration gives place to a yellow turbidity, and benzene appears on the surface of the liquid. On extraction with ether, the only products are benzene and azobenzene, no diazo-compound being formed. The same phenomenon is observed if equimolecular amounts of phenylhydrazine and oxygen (as Caro's acid) are used, or if the solutions are rendered slightly alkaline or acid before mixing. It appears highly probable that the greenish-yellow coloration is due to the presence of a hydroxyhydrazine as postulated by Chattaway, and that this then undergoes disruption into benzene and azobenzene.

No explanation is given by Chattaway of the mechanism by which azo-compounds are formed in the reaction, but it seems probable that two molecules of the hydroxyhydrazine may decompose according to the scheme:

$$\begin{matrix} R\cdot NH\cdot N \\ R\cdot NH\cdot N \end{matrix}\begin{matrix} H\cdot OH \\ H\cdot OH \end{matrix} \rightarrow \begin{matrix} R\cdot NH \\ R\cdot NH \end{matrix} + \begin{matrix} N \\ \| \\ N \end{matrix} + 2H_2O,$$

giving rise (in the case of phenylhydrazine) to hydrazobenzene which would be immediately oxidised to azobenzene.

Confirmation of this is perhaps furnished by Chattaway's isolation, in one experiment using 100 grams of phenylhydrazine, of a very small amount of a white, crystalline solid melting at 125°. As this substance was not recrystallised, it appears likely that it was hydrazobenzene, which melts at 131° [Gattermann (*Practical Methods of Organic Chemistry*) gives 126°].

69. "Some reactions of keten." By Frances Chick and Norman Thomas Mortimer Wilsmore.

No better source for the preparation of keten by the "pyrogenic" method than acetic anhydride has been found. With this substance a yield of about 10 per cent. of fairly pure keten is readily obtained. Acetone is more easily split up, but the resulting keten is too impure for most purposes. Glacial acetic acid is not attacked by the hot wire.

All attempts to prepare glycollaldehyde by the action of keten on water were unsuccessful, only acetic acid being formed. The aldehyde reactions previously mentioned (*Trans.*, 1907, **91**, 1941) were found to be due to traces of formaldehyde in the crude keten. Carefully fractionated samples of keten, such as those used for

analysis, did not give the aldehyde reactions. Similarly, with alcohol only ethyl acetate was formed.

Gaseous keten is slightly soluble at the ordinary temperature in benzene, chloroform, carbon tetrachloride, and ether, and very soluble in acetone and in acetic anhydride. Liquid keten is miscible without chemical reaction with most organic solvents which are liquid at its boiling point, including alcohol.

By the action of liquid hydrogen chloride on liquid keten at the ordinary temperature, acetyl chloride, boiling at 51—52°, was obtained. There was no sign of the presence of chloroaldehyde or of dichloroethyl acetate, but a small quantity of an oil with a terpene-like smell was obtained from the residue. In the same way with liquid hydrogen sulphide, thioacetic anhydride, boiling at 55—58°, was formed.

Keten does not react with oxamide, benzamide, nitrosoaniline, acetyl chloride, amyl nitrite, or ethyl iodide. Also, liquid keten does not react at the ordinary temperature with liquid cyanogen. It reacts slowly, however, with anhydrous hydrocyanic acid, but does not appear to form acetyl cyanide.

70. "Para- and meta-nitrosoacetanilide." By John Cannell Cain.

Para- and meta-nitrosoacetanilide have been prepared by oxidising the corresponding monoacetylphenylenediamine with Caro's acid.

p-*Nitrosoacetanilide* exists in two modifications: the unimolecular form is green, and melts at 176° with decomposition, whilst the bimolecular variety is colourless, and melts at 180—181° without decomposition.

This appears to be the first instance of both modifications of a nitroso-compound existing in the solid condition.

m-*Nitrosoacetanilide* also exists in two forms: the unimolecular modification, which was not isolated as it could not be obtained free from the bimolecular variety, remains as a green residue from its ethereal solution. This, on crystallisation from alcohol, furnishes the bimolecular form in pale, yellowish-brown needles melting at 111°.

71. "Labile isomerism among acyl-salicylamides and acyl-hydroxyamines." By Arthur Walsh Titherley.

A reply to Auwers' criticism (*Ber.*, 1907, **40**, 3506).

ADDITIONS TO THE LIBRARY.

By Purchase.

Grotthuss, *Theodor von.* Abhandlungen über Elektrizität und Licht. Edited by *R.* **Luther** and *Arthur von* **Oettingen.** (Ostwald's *Klassiker*, No. 152.) pp. 199. ill. Leipzig 1906. (*Recd.* 27/2/08.)

Herz, *W.* Physikalische Chemie als Grundlage der analytischen Chemie. (Die chemische Analyse, Vol. III.) pp. 114. Stuttgart 1907. (*Recd.* 19/2/08.)

Post, *Julius.* Chemisch-technische Analyse. Handbuch der analytischen Untersuchungen zur beaufsichtigung chemischer Betriebe. Edited by *Bernhard* **Neumann.** Vol. I, part 4. pp. 815 to 974. ill. Braunschweig 1908. (*Recd.* 30/1/08.)

Sella, *Quintino.* Abhandlungen zur Kristallographie. Edited by *F.* **Zambonini.** (Ostwald's *Klassiker*, No. 155.) pp. 44. Leipzig 1906. (*Recd.* 27/2/08.)

Sindall, *Robert Walter.* Paper technology. An elementary manual on the manufacture, physical qualities, and chemical constituents of paper and of paper-making fibres. pp. xv + 253. ill. London 1906. (*Recd.* 22/2/08.)

Thomsen, *Julius.* Thermochemistry. Translated from the Danish by *Katherine A.* **Burke.** pp. xv + 495. London 1908. (*Recd.* 15/2/08.)

LOTHAR MEYER MEMORIAL.

The Council has decided to make a donation of £10 to the Lothar Meyer Memorial Fund.

Many old pupils and admirers of the author of "Die Modernen Theorien der Chemie" may be desirous of contributing to this Memorial, and the Treasurer will be glad to receive, at an early date, subscriptions from Fellows and others to the Fund.

Cheques, &c., should be made payable to Dr. Alexander Scott, crossed "Lothar Meyer Memorial Fund A/c.," and sent to the Treasurer, Chemical Society, Burlington House, W.

At the next Ordinary Meeting, on **Thursday**, April 2nd, 1908, at **8.30** p.m., the following papers will be communicated:

"The condensation of epichlorohydrin with phenols." By D. R. Boyd and E. R. Marle.

"Rate of hydrolysis of chloroacetates, bromoacetates and α-chlorohydrin by water and by alkali, and the influence of neutral salts on the reaction velocities." (Preliminary note.) By G. Senter.

"A new general method of preparing diazonium bromides." By F. D. Chattaway.

"On the probable nature of the impurity found in the triphenylmethane spectrum." By W. N. Hartley.

"The absorption spectrum of triphenylmethane." By A. G. G. Leonard.

"The constituents of Cyprus origanum oil. Isolation of a new terpene (origanene)." By S. S. Pickles.

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Issued 29/4/08

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 24. **No. 340**

Thursday, March 26th, 1908, Annual General Meeting, Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

Dr. A. MCKENZIE and Dr. G. T. MORGAN were appointed Scrutators, and the ballot was opened for the election of Officers and Council for the ensuing year.

The PRESIDENT announced that communications from Professor W. J. Pope, Mr. John Allen, and Prof. Adrian J. Brown had been received, stating their unwillingness to accept nomination as Vice-President and as Ordinary Members of Council respectively.

The President presented the Report of the Council on the progress of the Society during the past twelve months, and the Treasurer gave a statement as to the Society's income and expenditure during the year 1907.

The adoption of the Report of the Council, together with the Balance Sheet and statements of Accounts for the year ended 31st December, 1907, was proposed by Professor A. LIVERSIDGE, seconded by Professor E. DIVERS, and carried unanimously.

A vote of thanks to the Auditors, which was proposed by Dr. ALEXANDER SCOTT, seconded by Mr. OTTO HEHNER, was acknowledged by Dr. H. FORSTER MORLEY.

REPORT OF THE COUNCIL.

As in recent years, the Council have the satisfaction of stating that the prosperity of the Society continues, both the number of papers read and the number of Fellows on the list showing a considerable increase.

On the 31st December, 1906, the number of Fellows was 2,860. During 1907, 137 Fellows were elected and 5 reinstated, making a gross total of 3,002. The Society has lost 30 Fellows by death; 30 have resigned; 1 election and 1 reinstatement have become void; 1 newly-elected Fellow has withdrawn, and the names of 43 Fellows have been removed from the list for non-payment of Annual Subscriptions.

The total number of Fellows, therefore, at the 31st December, 1907, was 2,896, showing an increase of 36 over the number for the previous year.

The names of the deceased Fellows, with the dates of their election, are:

A. C. Aitkin (1901).
T. Andrews (1870).
P. T. Austen (1877).
A. Bottle (1873).
W. Bowen (1903).
E. Chapman (1868).
E. D. Chester (1882).
J. Clark (1876).
George Davey (1893).
A. Dupré (1860).
J. Gale (1866).
Sir D. Gamble, Bart. (1851).
S. Hall (1876).
L. F. V. Harcourt (1863).
B. J. Harrington (1897).
J. Ince (1867).
F. Keeling (1883).
C. O'Sullivan (1876).
F. J. M. Page (1871).
A. C. Palmer (1906).
S. Parfitt (1906).
Sir W. H. Perkin (1856).
H. D. Perkins (1905).
B. C. Polkinghorne (1899).
W. Pritchard (1870).
R. R. Swann (1905).
J. F. Walker (1865).
R. Warington (1863).
H. A. Wetzel (1883).
H. E. Wright (1900).

The following Fellows have resigned:

A. Amos.
A. C. Benson.
T. H. Boardman.
J. Cameron.
J. Daniell.
T. Divine.
G. Dyson.
A. T. Eutroppe.
J. A. Fawcett.
G. Goldfinch.
W. F. Grace.
R. Grimwood.
W. B. Hards.
G. H. U. Harrow.
H. J. Hodges.
W. A. F. Lethbridge.
H. Martin.
H. G. F. Micklewright.
J. T. Nance.
D. Northall-Laurie.
A. N. Palmer.
E. W. Sawdon.
T. Steel.
S. D. Stennitt.
A. E. Tanner.
W. H. Templeman.
J. H. Wainwright.
J. W. Wells.
H. Wilson.
J. H. Wolfenden.

The number of those Fellows who were elected prior to 1860 has been still further diminished by the death of Sir David Gamble, Bart., who was elected on March 17th, 1851, and Sir William H. Perkin, who was elected on December 15th, 1856.

The number of Honorary and Foreign Members at the close of 1906 was 33. No elections have taken place during 1907, but the Society has to mourn the loss of Professor Marcellin Berthelot, elected March 1st, 1860, deceased March 18th; Professor Dr. Dmitri Ivanovitsch Mendeléeff, elected February 1st, 1883, deceased February 2nd; Professor Dr. Nicolai Menschutkin, elected January 20th, 1898, deceased February 5th; and Professor Henri Moissan, elected January 20th, 1898, deceased February 20th. The number of Honorary and Foreign Members, therefore, at the 31st December, 1907, was 29.

During the year 1907, 268 scientific communications have been made to the Society, 203 of which have been published already in the *Transactions*, and abstracts of all have appeared in the *Proceedings*.

The volume of Transactions for 1907 contains 2,089 pages, of which 2,021 are occupied by 205 memoirs, the remaining 68 pages being devoted to the Faraday Lecture, the Obituary Notices, the Report of the Annual General Meeting, and the Presidential Address; the volume for the preceding year contains 186 memoirs, which occupy 1,890 pages.

The Journal for 1907 contains also 4,686 abstracts of papers published mainly in foreign journals, which extend to 2,100 pages, whilst the abstracts for 1906 numbered 4,541, and occupied 1,912 pages.

The abstracts for 1907 may be classified as follows:

PART I.

	Pages.	No. of Abstracts.
Organic Chemistry	1,104	1,831

PART II.

General and Physical Chemistry		725
Inorganic Chemistry		622
Mineralogical Chemistry		117
Physiological Chemistry		545
Chemistry of Vegetable Physiology and Agriculture		244
Analytical Chemistry		602
	996	2,855
Total in Parts I. and II.	2,100	4,686

In the hope of diminishing the confusion which had arisen in the nomenclature of the proteins, consideration of the subject was undertaken by the Publication Committee, in conjunction with representatives of the Physiological Society; the joint committee concluded their deliberations early in 1907, and their recommendations appear in the Proceedings for that year.

Recognising the importance, from a public standpoint, of the Presidential Address delivered by Professor Meldola, F.R.S., in March, 1907, the Council have felt it desirable that his remarks on that occasion should attract the attention of a wider circle than is reached by the Society's Transactions; accordingly 5,000 copies of the address have been circulated among the members of various public bodies, including both Houses of Parliament, and the Council hope that this unusual step will have the effect of bringing the subject of Professor Meldola's discourse into suitable prominence.

During the past year, the Society has had to mourn the loss of Sir William Perkin, which took place on July 14th, 1907, just twelve months after the International Celebration which marked the Fiftieth Anniversary of the Foundation of the Coal Tar Colour Industry. This is not the place in which to deal with the splendid achievements of the late Past President, or the qualities which endeared him to the Fellows, who will remember with melancholy satisfaction that he lived to participate in the widely-supported public appreciation of the preceding year, and in the subsequent commemoration celebrated in the United States. The marble bust of Sir William Perkin has now been placed in the meeting room, and a large photograph of the portrait painted by Mr. A. S. Cope, A.R.A., is also the property of the Society, having been presented by Sir William a few months before his death.

In view of the losses incurred during recent years through the death of several Honorary and Foreign Members, thereby reducing the number of survivors to 29, the Council recommended for election the following distinguished chemists: Professor A. E. J. Gautier, Professor Albin Haller, Professor J. W. Hittorf, Professor J. A. Le Bel, Professor H. L. Le Chatelier, Professor T. W. Richards, and Professor Otto Wallach. This recommendation was duly ratified by the Society at the meeting on Thursday, February 6th, 1908.

An agreeable feature of the past year has been the Jubilee Celebration of the Société Chimique de France, and on that occasion an address of congratulation was presented by Sir William Ramsay, F.R.S., on behalf of the Society, which was represented also by Professor H. E. Armstrong, F.R.S., and Dr. Horace Brown, F.R.S.; a commemorative medal has been received from the French institution, and added to the Society's collection. A somewhat similar event took

place in September, when the Geological Society celebrated their Centenary, the President being again delegated to offer the felicitations of the Chemical Society. A copy of the recently compiled History of the Geological Society has been since presented to the Library.

Professor J. Bretland Farmer, F.R.S., accepted the invitation of the Council to deliver a discourse before the Society, and his lecture, entitled "Some Borderline Problems in Botany," was greatly appreciated by the Fellows.

Late in 1906, Geheimrat Professor Emil Fischer, F.R.S., an Honorary and Foreign Member since 1892, was nominated Faraday Lecturer, and gave his address, in German, on October 18th, 1907, in the theatre of the Royal Institution, kindly lent by the managers for the occasion; at the termination of the lecture, entitled "Synthetical Chemistry in its Relation to Biology," the Faraday Medal was presented to Professor Fischer by the President.

In common with all corporate bodies engaged in scientific pursuits, the Chemical Society has keenly deplored the death of Lord Kelvin, who, although not on the roll of Fellows, had been the guest of the Society on many occasions. At the request of the Council, the President transmitted to Lady Kelvin a resolution of sympathy, and the Society was represented at the funeral ceremony in Westminster Abbey.

Professor W. Wislicenus, of Tübingen, having initiated a memorial to the late Professor Lothar Meyer, the Treasurer was authorised to contribute from the funds of the Society, and the Council venture to hope that the memorial may be supported by individual Fellows.

The ventilation of the meeting room and council chamber has occupied the attention of the House Committee, who have recommended the installation of electric fans; since their report was received and adopted by the Council, a Fellow, who desires to remain anonymous, has most kindly undertaken to defray the cost of this highly necessary improvement.

In addition to an engraving of Daniell and Faraday, for which the Society is indebted to Professor Meldola, F.R.S., numerous articles of historical interest and value have come into the possession of the Society in virtue of a bequest by the late Professor Warington.

The number of books borrowed from the Library during 1907 was 1,317, as against 1,126 in the previous year. The additions to the Library comprise 138 books, of which 79 were presented, 401 volumes of periodicals (representing 243 journals), and 40 pamphlets, as against 121 books, 385 volumes of periodicals (representing 229 journals), and 32 pamphlets last year.

The experiment of opening the Library during Thursday evenings

other than those on which the Society meets has been discontinued, so few Fellows having used the Library on those occasions.

In May, 1907, a special leaflet was issued with the Journal indicating the parts required to complete certain sets of periodicals in the Library, in the hope that Fellows happening to possess copies of the desired numbers would present them to the Society. In response to that circular, donations were received from numerous Fellows, and this favourable response has encouraged the Council to hope that further contributions of a similar character may be added to the Library.

As was announced at the last Annual Meeting, the Society received from the Worshipful Company of Goldsmiths a munificent donation of £1,000 for the Research Fund. This fund has been still further increased by the handsome sum of £2,704 3*s.* 8*d.*, which was handed over to the Treasurer in July by the Perkin Memorial Fund Committee. These two sums, as now invested, have augmented the annual income of the Research Fund by £126 5*s.*, and will enable the Research Fund Committee in the present year to recommend the Council to make grants to the amount of £340 to £350. Of this sum, about £34 is more or less especially to be devoted to the encouragement of research in inorganic and metallurgical chemistry, and about £92 for investigations relating to problems connected with the coal-tar and allied industries.

In spite of several items of a somewhat exceptional nature, the Treasurer is glad to be able to report that he has a substantial surplus to carry forward as the result of the year's finance. The income of the Society from all sources for 1907 is £7,260 4*s.* 10*d.*, as against £7,121 8*s.* 11*d.* in 1906, and the expenditure is £6,750 8*s.* 5*d.*, instead of £6,379 15*s.* 9d., so that, whilst our expenditure has increased by £370 12*s.* 8*d.*, our income has only grown by £138 15*s.* 11*d.* This still leaves a surplus of £509 16*s.* 5*d.* on the year's working.

The increase in income may be put down almost entirely to the increase in Annual Subscriptions, for the increase of £100 in the Life Compositions is more than neutralised by the drop of £104 in Admission Fees.

The *Journal* and *Annual Reports* have cost respectively £182 19*s.* 8*d.* and £24 8*s.* 5*d.* more than last year, but a saving of £23 18*s.* has been effected on the *Proceedings* and the *List of Fellows.* The reprinting of certain numbers of the *Proceedings* which were "out of print" has put it within the power of Fellows to complete their sets of *Proceedings*, and the increase in the sale has already more than repaid the cost of the reprints.

A certain amount of redecoration beyond the annual cleaning, the balance of the Dinner account, and the printing and distribution of

5,000 copies of last year's Presidential Address are the chief items which have raised the "administrative expenses" so much above those of last year.

In July the Treasurer was able to purchase £1,200 North British Railway 3 per cent. Debenture Stock; a glance at the balance sheet will show that the value of the invested capital of the Society was on December 31st, 1907, £18,362 9*s.* 9*d.*, and that of the Research Fund, £10,016 11*s.* 10*d.*

A vote of thanks to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year was proposed by Dr. FRANK CLOWES, seconded by Dr. W. E. ADENEY, and unanimously adopted. Professor J. EMERSON REYNOLDS responded.

The President then delivered his address entitled "The Electron as an Element."

Professor RAPHAEL MELDOLA proposed a vote of thanks to the President for his address and for his services in the Chair during the past year, coupled with the request that he would allow the address to be printed in the *Transactions* of the Society. Dr. RUDOLPH MESSEL seconded the motion, which was put to the Meeting and carried with acclamation.

The Report of the Scrutators was presented to the President, who declared the following to have been elected as Officers and Council for the ensuing year:

President: Sir William Ramsay, K.C.B., F.R.S.

Vice-Presidents who have filled the Office of President: H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, D.Sc., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; A. G. Vernon Harcourt, M.A., D.C.L., F.R.S.; Raphael Meldola, F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.A., M.B., F.R.S.; J. Emerson Reynolds, Sc.D., M.D., F.R.S.; Sir Henry E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; T. E. Thorpe, C.B., LL.D., F.R.S.; W. A. Tilden, D.Sc., F.R.S.

Vice-Presidents: J. Campbell Brown, D.Sc., LL.D.; J. J. Dobbie, M.A., D.Sc., F.R.S.; F. Stanley Kipping, D.Sc., Ph.D., F.R.S.; Rudolph Messel, Ph.D.; Sir Alexander Pedler, C.I.E., F.R.S.; W. H. Perkin, Ph.D., F.R.S.

Treasurer: Alexander Scott, M.A., D.Sc., F.R.S.

Secretaries: M. O. Forster, D.Sc., Ph.D., F.R.S.; A. W. Crossley, D.Sc., Ph.D., F.R.S.

Foreign Secretary: Horace T. Brown, LL.D., F.R.S.

Ordinary Members of Council: Julian L. Baker; George T. Beilby, F.R.S.; Alfred C. Chapman; Julius B. Cohen, Ph.D., B.Sc.; J. T. Hewitt, M.A., D.Sc., Ph.D.; W. R. E. Hodgkinson, Ph.D.; H. A. D. Jowett, D.Sc.; H. R. Le Sueur, D.Sc.; F. E. Matthews, Ph.D.; A. G. Perkin, F.R.S.; W. J. Sell, Sc.D., F.R.S.; John Wade, D.Sc.

Thursday, April 2nd, 1908, at 8.30 p.m., Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

Messrs. H. Bassett, jun., H. T. Clarke, and C. Dickinson were formally admitted Fellows of the Society.

It was announced that the Council had appointed the following Committees for 1908—1909:

Finance Committee: Messrs. E. G. Hooper, G. T. Moody, T. E. Thorpe, W. A. Tilden, and the Officers.

House Committee: Messrs. W. R. Dunstan, J. E. Reynolds, W. J. Russell, J. M. Thomson, T. E. Thorpe, W. A. Tilden, and the Officers.

Library Committee: Messrs. E. C. C. Baly, B. H. Brough, F. D. Chattaway, B. Dyer, A. Harden, C. A. Keane, A. Lapworth, E. J. Mills, J. M. Thomson (*Chairman*), J. A. Voelcker, J. Wade, the Editor, and the Officers.

Publication Committee: Messrs. E. C. C. Baly, W. R. Dunstan, J. T. Hewitt, R. Meldola, G. T. Morgan, T. E. Thorpe, J. Wade, and the Officers.

Research Fund Committee: Messrs. G. T. Beilby, P. F. Frankland, A. D. Hall, G. Matthey, R. Meldola, R. Messel, W. H. Perkin, J. E. Reynolds, W. A. Tilden, Sir A. Pedler, and the Officers.

Certificates were read for the first time in favour of Messrs.:

Donald Francis Blyther, B.Sc., 77, Knights Road, Silvertown, E.
Henry Brougham Hutchinson, Ph.D., Ashby Villa, Devonshire Road, Harpenden.
Stanley Allen Warrington Okell, 27, King's Road, Ealing, W.
John Day Speed, Mill House, Enfield Lock, Middlesex.

Certificates have been authorised by the Council for presentation for ballot under Bye-Law I (3) in favour of Messrs. :

Cyril Arden Hinds, 724, Russell Street, Bristol, Tenn., U.S.A.
William Seelhorst, Eastern Smelting Co., Ltd., Penang, Straits Settlements.

Of the following papers, those marked * were read :—

*72. "**Rate of hydrolysis of chloroacetates, bromoacetates, and α-chlorohydrin by water and by alkali, and the influence of neutral salts on the reaction velocities.**" (**Preliminary note.**) **By George Senter.**

In a former paper (*Trans.*, 1907, **91**, 460), the results of an investigation of the rate of hydrolytic decomposition of certain chloroacetates by water and by alkali were given, and the effect of certain neutral salts on the rate of reaction was discussed. The rate of displacement of halogen by hydroxyl under different conditions has now been investigated for bromoacetic acid and sodium bromoacetate and for α-chlorohydrin, and the effect of certain neutral sodium salts on the reaction velocities has been examined.

Bromoacetic Acid.—The reaction represented by the equation $CH_2Br{\cdot}CO_2H + H_2O = HO{\cdot}CH_2{\cdot}CO_2H + HBr$ is unimolecular, and the value of $k = 1/t \log C_o/C_t$ is 0·0062 at 102°, as compared with $k = 0{\cdot}00048$ for chloroacetic acid under equivalent conditions. The reaction is slightly retarded by hydrogen bromide.

Sodium Bromoacetate. — The reaction $CH_2Br{\cdot}CO_2Na + H_2O = HO{\cdot}CH_2{\cdot}CO_2H + NaBr$ is unimolecular in dilute solution ; the value of $k = 1/t \log C_o/C_t$ at 102° is 0·020. The hydrolysis of this salt by alkali, represented by the equation $CH_2Br{\cdot}CO_2Na + NaOH = HO{\cdot}CH_2{\cdot}CO_2Na + NaBr$, is bimolecular, and at 70·4° $k = \frac{1}{tC_o} \cdot \frac{C_t}{(C_o - C_t)}$ has the value 0·0314 when referred to a $N/10$ solution.

Effect of Temperature.—The average velocity quotients for a rise of temperature of 10° between the limits of temperature given are as follows. Chloroacetic acid and water (70—100°), 2·6 ; sodium chloroacetate and water (70—100°), 3·2 ; sodium chloroacetate and hydroxide (70—100°), 2·5 ; bromoacetic acid and water (70—100°), 2·4 ; sodium bromoacetate and water (70—100°), 2·9 ; sodium bromoacetate and hydroxide (30—70°), 2·75. The fact that the temperature-coefficients of the hydrolysis of sodium chloroacetate by water and by alkali are different, shows that the assumption often made, that the OH′ ions in the latter case act in a catalytic manner, is not justified, and

supports the views on the mechanism of the reactions advanced in the previous paper (*loc. cit*).

α-Chlorohydrin.—The hydrolysis of α-chlorohydrin by water alone is extremely slow; the value of $k = 1/t \log C_0/C_t$ is 0·00010 at 101°. Hydrochloric acid retards the reaction slightly. In the presence of alkali, the change is extremely rapid; the value of k for the bimolecular reaction represented by the equation $HO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2Cl + NaOH = HO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH + NaCl$ is 0·052 at 0°, referred to a $N/10$ solution as unit.

Effect of Neutral Salts.—Neutral sodium salts slightly retard the hydrolysis of chloro- and bromo-acetates by water, they greatly accelerate the hydrolysis of these compounds by alkali, but have practically no effect on the rate of reaction between α-chlorohydrin and alkali. The accelerating effect of molar concentrations of different salts on 0·1 molar solutions of chloro- or bromo-acetates and alkali is represented in the table, the rate of the reaction in the absence of neutral salts being taken as unity.

Sodium Chloroacetate and Hydroxide at 70·4°:

Neutral salt	none	$NaNO_3$	NaCl	$NaClO_3$	$\frac{1}{2}Na_2SO_4$	$CH_3{\cdot}CO_2Na$	$H{\cdot}CO_2Na$
Ratio of velocities	1·0	1·55	1·55	1·55	1·55	1·58	3·3

Sodium Bromoacetate and Hydroxide at 70·4°:

Neutral salt	none	$NaNO_3$	NaBr	$NaClO_3$	$H{\cdot}CO_2Na$
Ratio of velocities ...	1·0	1·53	1·53	1·53	2·8

The effect of sodium nitrate on the reaction between sodium chloroacetate and hydroxide is of the same magnitude, within the limits of experimental error, at 55° and 101°.

The above results confirm the views on neutral salt action advanced in the previous paper, that the effect in question is mainly due to the action of the salt on the reacting substances, and appear to be in compatible with the hypothesis advocated from time to time by different observers, most recently by Armstrong and his co-workers (*Proc. Roy. Soc.*, 1907, **79**, *A*, 586), that neutral salt action is due to combination between salt and solvent, with consequent concentration of the solution.

Discussion.

Mr. Jeffers asked if Dr. Senter assumed that the pressure developed in the sealed tubes had no influence whatever on the velocity of hydrolysis. Pressure was known to have a large influence in the case of the hydrolysis of carbohydrates, and it seemed impossible to correlate the figure given for the velocity unless the pressure was known in all cases.

Dr. SENTER, in reply, pointed out that, according to the experiments of Röntgen (*Ann. Physik*, 1891, **45**, 98; compare also Rothmund, *Zeitsch. physikal. Chem.*, 1896, **20**, 170), the effect even of great changes of pressure on the rate of a reaction was very slight. In the case most fully investigated, a change of pressure from 1 to 500 atmospheres increased the rate of the reaction by 1 per cent. As in the present experiments the highest pressure in the sealed tubes was 2 atmospheres and the variations less than 1 atmosphere, it was obvious that the effect in question was quite negligible.

***73. "The constituents of Cyprus origanum oil. Isolation of a new terpene 'origanene.'" By Samuel Shrowder Pickles.**

The essential oil yielded by the principal origanum plant of Cyprus has been examined and found to consist mainly of carvacrol (84 per cent.). There are also present (1) a hydrocarbon, $C_{10}H_{16}$, apparently a new terpene, for which the name *origanene* is proposed (2·5 per cent.); (2) cymene, which, together with associated terpenes (b. p. 170—180°), constitutes 8·5 per cent.; (3) terpene alcohols (3·5 per cent.), and (4) high boiling residue (1·3 per cent.), besides very small quantities of a second phenol which gives a purple coloration with ferric chloride, and a volatile acid, probably *iso*butyric acid.

The results of experiments on the constitution of the hydrocarbon "origanene" lead the author to conclude that the terpene is probably $\Delta^{1:3}$-p-*menthadiene*, $CMe\begin{matrix}CH{-}CH\\ CH_2{\cdot}CH_2\end{matrix}C{\cdot}CHMe_2$.

***74. "The displacement of halogen in *l*-phenylchloroacetic acid by hydroxy- and methoxy-groups. A contribution to the chemistry of the Walden inversion." By Alex. McKenzie and George William Clough.**

The authors have resolved *r*-phenylchloroacetic acid into its optically active components by means of morphine in methyl-alcoholic solution.

The action of water on *l*-phenylchloroacetic acid, the action of water on sodium *l*-phenylchloroacetate, the action of aqueous sodium hydroxide on sodium *l*-phenylchloroacetate, the action of water on silver *l*-phenylchloroacetate, the action of silver carbonate on *l*-phenylchloroacetic acid, and the action of methyl-alcoholic sodium methoxide on *l*-phenylchloroacetic acid have been examined with reference to the Walden inversion.

Discussion.

Dr. Smith, referring to the fact that *d*-chlorosuccinic acid is converted by sodium hydroxide into *l*-malic acid and by silver oxide into *d*-malic acid, stated that Walden assumes that the inversion, which must have occurred during one of these changes, takes place in the second reaction. In view of Dr. Senter's result, that sodium chloroacetate and sodium hydroxide react ionically, the converse would seem to be more probable, for during the reaction between sodium hydroxide and *d*-chlorosuccinic acid, which by analogy is ionic, there would be a greater possibility for change of configuration to occur than in the reaction between *d*-chlorosuccinic acid and silver oxide, which would be a case of simple substitution.

Dr. McKenzie stated that Walden regarded the change

$$d\text{-}CO_2H\cdot CH_2\cdot CHCl\cdot CO_2H \longrightarrow l\text{-}CO_2H\cdot CH_2\cdot CH(OH)\cdot CO_2H$$

by means of potassium hydroxide as, in all probability, optically normal, because the rotation of the malic acid formed is of the same sign as that of the malic acid from which *d*-chlorosuccinic acid is formed by the action of phosphorus pentachloride.

Fischer had pointed out (*Ber.*, 1907, **40**, 490) that the view that silver oxide acts abnormally, whilst potassium hydroxide acts normally, may appear somewhat strange to many chemists.

75. "The condensation of epichlorohydrin with phenols." By David Runciman Boyd and Ernest Robert Marle.

The authors find the statements of Cohn and Plohn (*Ber.*, 1907, **40**, 2597) with regard to the products obtained by the action of epichlorohydrin on alkaline solutions of phenol and *p*-cresol to be incorrect. The crystalline compound (m. p. 81—82°) which is obtained from phenol and epichlorohydrin, and which is stated by Cohn and Plohn to be phenyl glycide ether, $C_6H_5\cdot O\cdot CH_2\cdot CH\langle\begin{smallmatrix}CH_2\\O\end{smallmatrix}$, is really glyceryl diphenyl ether, $C_6H_5\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot O\cdot C_6H_5$.

Phenyl glycide ether is an oil boiling at 133° under 23 mm. pressure.

Similarly, the crystalline compound (m. p. 88°) obtained from *p*-cresol and epichlorohydrin is the glyceryl di-*p*-tolyl ether, $C_7H_7\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot O\cdot C_7H_7$, and not the *p*-tolyl glycide ether.

The authors have prepared *phenoxydichloropropane*, an oil boiling at 139—140° under 13 mm. pressure.

76. "A new general method of preparing diazonium bromides." By Frederick Daniel Chattaway.

Primary aromatic hydrazines react quantitatively with the diazonium perbromides producing diazonium bromides, thus:

$$2\begin{matrix}R\cdot N\cdot Br\\ |\\ Br\cdot N\cdot Br\end{matrix} + \begin{matrix}R\cdot N\cdot H\\ |\\ H\cdot N\cdot H\end{matrix} = 3\begin{matrix}R\cdot N\cdot Br\\ |\\ H\cdot N\cdot Br\end{matrix} = 3\begin{matrix}R\cdot N\cdot Br\\ \|\\ N\end{matrix} + 3HBr.$$

As the diazonium perbromides are so easily obtained in the solid state by adding bromine to aqueous solutions of diazonium salts, and as they can be kept in a dry atmosphere for a long time without alteration and are comparatively safe to handle, this reaction affords a very convenient method for preparing diazonium bromides in the solid state.

For this purpose, it is only necessary to suspend the finely-powdered perbromide in alcohol and, after cooling, to add the calculated quantity of the corresponding hydrazine also dissolved in alcohol and cooled. The solid diazonium bromide is at once formed, and, after adding an equal bulk of ether to complete the deposition, can be collected in a pure state.

The reaction is a general one, and takes place readily and quantitatively with all primary aromatic hydrazines and perbromides that have been studied.

77. "The absorption spectrum of triphenylmethane." By Alfred Godfrey Gordon Leonard.

In order to ascertain the cause of the difference between the absorption curve plotted by Hartley, in 1887, and that plotted by Baker, in 1907, the absorption spectrum of triphenylmethane was thoroughly re-examined.

All the specimens examined gave at first curves similar to that obtained in 1887, but, on purifying the samples by repeated recrystallisation from alcohol, the absorption curve became identical with that found by Baker. This curve is therefore the true absorption curve of triphenylmethane.

The difference is clearly shown to be caused by the presence of an impurity in the sample originally examined, and this impurity is always present when the triphenylmethane is prepared from benzene and chloroform by Friedel and Crafts' reaction (see following abstract).

78. "The nature of the impurity found in preparations of triphenylmethane." By Walter Noel Hartley.

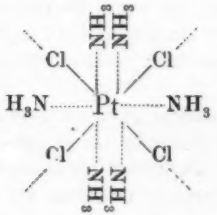
The experiments of Mr. A. G. G. Leonard have shown conclusively that in the preparation of triphenylmethane there are always two substances obtained, even when the materials are of the greatest purity and free from moisture.

The second substance must be a hydrocarbon; it is yellow, and apparently it undergoes oxidation, becoming still brighter in colour. From these and other considerations, it appears to be identical with Gomberg's triphenylmethyl, and the final product, with triphenylmethyl peroxide.

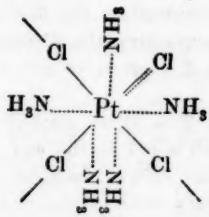
79. "The constitution of co-ordinated compounds." By Samuel Henry Clifford Briggs.

An attempt has been made to devise formulæ for co-ordinated compounds which will fulfil the requirements of the experimental results of Werner and his colleagues, and also give some idea of the manner in which the affinities of the atoms are disposed within the molecule.

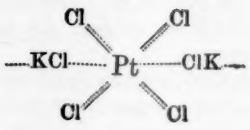
The existence of the two compounds $(Pt6NH_3)Cl_4$ and $(PtCl_6)K_2$, in which the platinum atom is the basis of a complex cation and anion respectively, suggests the view that the platinum atom has both positive and negative affinities (compare Berzelius, Abegg, and others). Assuming that every element has two kinds of affinity, $(Pt6NH_3)Cl_4$, may be written:



in which the saturation of the positive affinity of the platinum (situated at the centre of an octahedron) is expressed by a straight line, and the saturation of the negative affinity by a dotted line. On removing one molecule of ammonia and saturating the negative affinity of the platinum thus liberated by the free positive affinity of one of the chlorine atoms, we obtain (I). Similarly, $(PtCl_6)K_2$ is represented by (II).



(I.)



(II.)

These bonds are intended to represent the saturation of affinities only, and no assumptions are made with reference to the valencies of the atoms in question.

The formulæ were discussed from the point of view of the electrolytic dissociation of the compounds, and it is suggested that the non-ionisable chlorine atom in the compound $(Pt5NH_3Cl)Cl_3$ is the one which has both the negative and positive affinities saturated as expressed in the formula given above.

In the salts with a complex anion, these formulæ suggest the possibility of isomerism due to differences in the points of attachment of the positive atoms. The cases of isomerism in compounds with an anionic complex, which are referred to by Werner (*Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*), can thus be satisfactorily explained.

80. "A combined stopcock and capillary connecting tube for gas burettes." By Arthur Edwin Hill.

The familiar method of connecting a Hempel burette to the absorption pipette by means of a short piece of thick-walled glass capillary tubing bent twice at right angles and two short pieces of thick rubber tube is very unsatisfactory, as it is liable to give inaccurate results, and requires a great deal of attention.

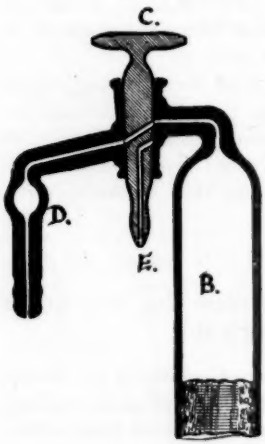
Before commencing an absorption, the air, entrapped in the capillary tubes and rubber connexions, should be expelled; as this operation is rather troublesome, it is often not properly effected. Again, when absorption is complete in the pipette and the gas is returned to the measuring burette, the absorbent should be allowed to flow back as far as the capillary tube at the top of the burette, but, since this adjustment has to be made when the thread of absorbent is out of sight behind the rubber connexion, some of it often finds its way into the burette before the pinchcock can be closed.

The combined stopcock and capillary connecting tube indicated in section in the figure is sealed to the top of the measuring burette *B*.

The three-way stopcock *C*, in addition to controlling the flow of gas from the burette, also affords a means of connecting the pipette with the outside air through the bottom outlet *E* when it is attached to the burette.

The burette is connected to the pipette by a short piece of thick rubber tube, which is slipped over and well wired to the end of the capillary connecting tube and to the capillary tube of the pipette.

To expel the air entrapped in the capillary tubes and rubber connexion, a piece of rubber tube is slipped over the bottom outlet *E* of the stopcock *C*, and the stopcock is turned to make connexion between the pipette and the outside air; the air is then sucked out through the tube, and the absorbent fills the vacant space. The stopcock is closed by giving it a half turn, so that the handle is in a plane at right angles to that of the connecting tube. In order to connect the burette with the pipette, the stopcock is given another half turn in the same direction as before. The barrel of the stopcock is pierced in a way which makes it impossible to connect the burette with the outside air through the bottom outlet *E*, a source of accidental error being thereby eliminated.



When absorption is complete and the gas is returned to the burette, the absorbent is allowed to flow back as far as the stopcock *C*, which is quickly closed to prevent it from flowing any further. The bulb *D* facilitates this adjustment by retarding the advance of the absorbent before it reaches the stopcock; it also prevents the drops of absorbent, which often lodge in the rubber connexion, from passing over with the gas into the burette.

Before the pipette is disconnected from the burette, the stopcock is turned back to the position which will connect the pipette with the outside air, and the thread of absorbent is allowed to flow back into the pipette. They are then disconnected, and those parts of the capillary connecting tube and stopcock which have been in contact with the absorbent can be washed with water and subsequently dried in a current of warm air without in any way affecting the contents of the burette.

Subsequent absorptions are effected by a similar procedure.

81. "The hydrolysis of amygdalin by emulsin. Part I." By Samuel James Manson Auld.

By means of specially devised apparatus, the hydrolysis of amygdalin by emulsin has been studied in detail by estimating the hydrocyanic acid produced during the reaction. It has been shown that Jorissen and Hairs' "emulsin" is really a mixture of two enzymes, namely, true emulsin and a maltase-like ferment. The effect of varying the concentration of amygdalin and emulsin has been investigated, as also the action of many inhibitants. Of particular importance is the fact elucidated that the activity of emulsin is intimately bound up with basic a d acidic groups, as both acids and alkalis only render the ferment inactive and do not destroy it except in high concentrations. Contrary to the statements of Tammann, the decomposition of amygdalin by emulsin nearly approaches completion, as much as 97 per cent. of the available glucoside being decomposed as measured by the hydrocyanic acid formed. The end-point of the reaction has been found to be independent of the temperature, and the the temperature-coefficients of the action have been measured over a range of 45°.

82. "Complex nitrites containing potassium and lead. (Preliminary note.)" By Andrew Norman Meldrum.

The reaction between potassium nitrite and a lead salt (which may be the acetate, nitrate, chloride, bromide, or iodide) results in the production of complex compounds, which, in addition to potassium, lead, nitrosyl, and water, may contain one or more equivalents of the negative ion with which the lead was originally associated. The products vary in colour from bright yellow to orange, and they contain potassium and lead, as a rule, in the atomic ratio of 3 : 2.

In attempting to prepare the compound $K_2Pb(NO_2)_2(NO_3)_2,H_2O$, ($KO,NO_3,PbO,NO_5 + HO$, Hayes, *Quart. Journ. Chem. Soc.*, 1860, **13**, 335), the author finds that the product has always the composition, approximately, if not exactly, $K_2Pb(NO_2)_3NO_3,H_2O$.

Metallic lead is more easily attacked by solution of lead nitrate to which potassium nitrate has been added than by lead nitrate solution alone.

83. "The composition and formula of Wells' potassium lead periodide." By Andrew Norman Meldrum.

A potassium lead periodide has been described by Wells (*Amer. J. Sci.*, 1893, **46**, 190), who assigned to it the formula $K_3Pb_2I_8,4H_2O$,

analogous to that of the perbromide, $K_3Pb_2Br_8,4H_2O$, described in the same paper. Actually, the analyses of six different preparations of the substance were in good agreement with one another, and with the formula $K_9Pb_4I_{19},10H_2O$. In arriving at the formula $K_3Pb_2I_8,4H_2O$, Wells made the assumption that the material analysed was "contaminated with about 16·5 per cent. of potassium iodide, and that an excess of water was present, possibly on account of the hygroscopic properties of that salt."

Potassium iodide (150 grams), lead iodide (4 grams), iodine (70 grams), and water (90 c.c.) were mixed, and the mixture was slowly heated to the boiling point and filtered to remove any undissolved lead iodide. After some time, crystals separated, which were collected, drained on a porous tile, and exposed to the air until the odour of iodine was very faint. The product consisted of shining *violet* prisms, not unlike potassium permanganate, and hardly corresponded with Wells' "brilliant *black*, prismatic crystals."

The substance was analysed by methods different from those used by Wells. The lead and potassium were determined together as the sulphates, and the lead separately as chromate. Thiosulphate solution was used to determine (1) the total iodine (after addition of sulphuric acid and ferric alum, with subsequent distillation), and (2) the "extra" iodine. Water and "extra" iodine were determined together as loss on heating at 100°.

Found: mixed sulphates = 53·14, 52·97; Pb = 21·71, 21·67; total iodine = 64·19; "extra" iodine = 6·76, 6·81; loss at 100° = 11·33, 11·04.

$K_9Pb_4I_{19},10H_2O$ requires mixed sulphates = 52·97; Pb = 21·95; total iodine = 63·96; "extra" iodine = 6·74; loss at 100° = 11·52 per cent.

Potassium iodide, if present in a mixture to the extent of 16·5 per cent., the assumption which Wells makes, would surely be visible to the naked eye, but the material which the author analysed, when examined under the microscope, had all the appearance of a single substance, and it was not hygroscopic. The formula of the periodide is therefore $K_9Pb_4I_{19},10H_2O$, and it is probable that Wells, in assigning similar formulæ to the perbromide and the periodide, was led astray by the desire for uniformity.

84. "The molecular complexity of amides in various solvents." By Andrew Norman Meldrum and William Ernest Stephen Turner.

The authors have determined the molecular complexity by the boiling point method of eleven amides, namely, benzamide, salicyl-

amide, acetanilide, benzanilide, acetamide, monochloroacetamide, dichloroacetamide, trichloroacetamide, trichlorolactamide, carbamide, and malonamide in six solvents, so far as the solubility of the amides would allow (compare *Proc.*, 1907, **23**, 165). The Lumsden-Walker apparatus was employed, and the boiling points were specially corrected for the mere pressure effect of the accumulation of liquid in the boiling tube. The following table summarises the results, and includes also the dielectric constants of the solvents :

Solvent.	Benzene.	Ether.	Chloroform.	Acetone.	Alcohol.	Water.
Number of amides investigated...	8	5	9	10	11	9
,, ,, which form simple molecules	1 doubtful	1	2	9	9	4 and 1 doubtful
,, ,, which form associated molecules	7	4	7	1	2 doubtful	4
Dielectric constant of solvent ...	2·3 at 18°	4·4 at 18°	5 at 22°	25 at 20°	26 at 20°	80 at 17°

Except in the case of water, these results are in good accordance with the Nernst-Thomson theory that the smaller the dielectric constant of the solvent the greater is the association of the solute. Association in ether tends to be less than in benzene and much the same as in chloroform, just as would be inferred from the dielectric constant. Ether has hitherto been regarded as a non-associating solvent. In investigations into the physical properties of the amides and allied compounds, the most suitable solvent is alcohol, in which association is at a minimum.

Benzamide, salicylamide, acetanilide, and dichloroacetamide, the only instances of the kind known to the authors, have a greater molecular complexity in water than in alcohol. This is quite contrary to what would be expected from the Nernst-Thomson theory.

85. "The optical activity of compounds having simple molecular structure." By William Jackson Pope and John Read.

The authors described crystalline salts formed by chlorosulphoacetic acid and chlorobromomethanesulphonic acid with the optically active alkaloids, strychnine and quinidine. The two acids each contain an asymmetric carbon atom in the molecule, but, although their strychnine and quinidine salts crystallise well, no evidence was obtained that the acids are resolvable into enantiomorphously related components.

86. "Acetylketen: a polymeride of keten." By Frances Chick and Norman Thomas Mortimer Wilsmore.

It has been shown (*Nature*, 1907, **75**, 510; *Trans.*, 1907, **91**, 1938) that keten, both in the liquid and the gaseous states, condenses at the ordinary temperature to form a pungent-smelling, brown liquid. The latter has now been further studied. On distillation, a colourless liquid passes over, leaving a brown, non-volatile residue. This liquid boils at 126—127°, and solidifies in a freezing mixture to a white solid, which melts at −7° to −6°. It has an extremely pungent smell, suggestive both of acetic anhydride and of acrolein. On standing, even in absence of air, it slowly turns brown. Analysis gave C = 56·9, H = 5·0, whilst the depression of the freezing point of benzene and the vapour density, determined by Guy Lussac's method, agreed in giving a molecular weight of nearly 85, showing that the substance has the composition $C_4H_4O_2$, which requires C = 57·1; H = 4·8 per cent. M.W. = 84.

The liquid dissolves slowly in water, forming a strongly acid solution, which gives a violet colour with ferric chloride; on boiling the aqueous solution, carbon dioxide and acetone (recognised by the iodoform, benzaldehyde, and alkaline mercuric chloride reactions) are formed, and the solution becomes neutral. Hydrogen chloride facilitates the dissolution and decomposition. On boiling the substance with aqueous alkalis, acetates are formed, hence the substance combines with water to form acetoacetic acid. It reacts vigorously with aniline, forming acetoacetanilide melting at 84°.

The new substance is therefore *acetylketen*, having the formula $CH_3{\cdot}CO{\cdot}CH{:}CO$ or $CH_2{:}C(OH){\cdot}CH{:}CO$.

It reacts with two molecular proportions of phenylhydrazine, forming the colourless *phenylhydrazone-phenylhydrazide*, which melts at 152—153°.

87. "Saponification of ethyl formate by water in presence of acids as catalytic agents." By Arthur Lapworth.

Some statements in a recent paper by Stieglitz (*Amer. Chem. J.*, 1908, **39**, 402) have led the author to re-examine a suspicion, which he had some reason to entertain some six years ago, but which he did not then succeed in fully confirming. In recent experiments the velocity of saponification of ethyl formate in acetone solution has been measured, hydrogen chloride being used as catalyst, and the water being present in quantity small enough to be comparable with that of the ester.

Set I.—
A = 10 c.c. ethyl formate, 2 c.c. water, made up with acetone to 50 c.c.
B = 10 c.c. ethyl formate, 5 c.c. water, made up with acetone to 50 c.c.

Titre of 5 c.c. :

t =	0.	4′.	10′.	27′.	59′.	2h 58′.	6h 28′.	22h 30′
A =	(4·8)	6·1	7·5	10·45	16·35	36·3 (?)	41·40	43·2 c.c.
B =	(4·8)	6·55	7·4	9·75	15·2	28·50 (?)	42·4	57·0 ,,

Set II.—
C = 10 c.c. ethyl formate, 5 c.c. water, made up with acetone to 50 c.c.
D = 10 c.c. ethyl formate, 10 c.c. water, made up with acetone to 50 c.c.

Titre of 5 c.c. :

t =	0.	1′.	6′.	29′.	2h 0′.	9h 18′.	21h 9′.
C =	(2·5)	2·7	3·3	5·85	16·05	51·0	62·6 c.c.
D =	(2·5)	2·5	3·0	5·75	15·8	48·9	72·5 ,,

Set III.—
E = 5 c.c. ethyl formate, 5 c.c. water, made up with acetone to 50 c.c.
F = 10 c.c. ethyl formate, 5 c.c. water, made up with acetone to 50 c.c.

Titre of 5 c.c. :

t =	0.	2′.	25′.	54′.	1h 5′.	1h 31′.	6h 20′.	18h 50′.
E =	(4·0)	4·15	6·7	9·65	11·1	14·4	32·8	42·8 c.c.
F =	(4·0)	4·4	8·45	15·10	17·95	25·45	53·7	65·1 ,,

The alkali used was about $N/10$, but was somewhat stronger in the case of Set I. The numbers under $t = 0$ indicate about the amount of each titre due to hydrochloric acid used as catalyst in each set.

The results show clearly enough that, in the circumstances specified, the velocity of saponification is nearly independent of the concentration of the water present during a considerable part of the change, but that, when the mixture approaches equilibrium conditions, divergence is noticed for the first time.

Stieglitz has shown (*loc. cit.*, p. 417) that his own theory leads to the expression

$$\frac{dx}{dt} = K \times k \times C_{\text{ester}} \times C_{\text{H}} \times [C_{\text{H}} \times C_{\text{OH}}]$$

or

$$= \text{proportional to } C_{\text{ester}} \times C_{\text{H}} \times C_{\text{water}}^{2}$$

and is therefore incorrect.

This chemist is also incorrect in asserting that the author's own theory (Mellor, *Chemical Studies and Dynamics*, p. 289) fails to account for the catalysis of esters by hydrogen ions; it remains the only theory

in accordance with the facts, in spite of Stieglitz's remarks on the velocity of "salt formation" (*loc. cit.*, p. 425). It accounts for the dependence of the equilibrium condition on the concentration of the water, and the independence of the initial velocity of hydrolysis on that factor.

The author intends to continue with his colleague, the above work, and to study the influence of the concentration of alcohol and carboxylic acid on the velocity of esterification, as well as a number of analogous cases in which the influence of the substance generally used as solvent, is not fully understood.

88. "The triazo-group. Part III. Bistriazo-derivatives of ethane and of acetic ester." By Martin Onslow Forster, Hans Eduard Fierz, and Walter Philip Joshua.

1 : 2-*Bistriazoethane*, $N_3 \cdot CH_2 \cdot CH_2 \cdot N_3$, prepared from ethylene dichloride and sodium azide, is a colourless, refractive liquid which boils at 53° under 9 mm. pressure, and has sp. gr. 1·178 compared with water at 19°; the odour resembles that of chloroform, and the vapour is explosive. Stannous chloride liberates two-thirds of the nitrogen, giving ethylenediamine; alcoholic alkali does not set free nitrogen, but slowly eliminates hydrazoic acid.

The *compound*, $C_{14}H_{16}N_6$, which probably has the constitution

$$C_6H_5 \cdot NH \cdot N{:}N \cdot CH_2 \cdot CH_2 \cdot N{:}N \cdot NH \cdot C_6H_5,$$

arises by the action of magnesium phenyl bromide on 1 : 2-bistriazoethane, and crystallises from petroleum in lustrous, square plates with brown tinge; it melts at 128°, evolving gas with vigour. Dilute mineral acids liberate two-thirds of the nitrogen, producing aniline.

Bistriazoacetic ester, $CH(N_3)_2 \cdot CO_2 \cdot C_2H_5$, produced from dichloroacetic ester and sodium azide, is a colourless liquid which boils at 70—72° under 2 mm. pressure, and has sp. gr. 1·222 compared with water at 18°; the odour is scarcely perceptible. The ester is highly explosive, and liberates nitrogen explosively when treated with sulphuric acid. Hydrazoic acid is eliminated by alcoholic ammonia, consequently bistriazoacetamide could not be obtained.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

American Journal of Science and Arts. 2nd Series, Nos. 58—60, 77, 78, 94, 146—150. 3rd Series, Nos. 2—6. New Haven 1855—1871. (*Reference.*) From the Editor.

Society of Chemical Industry. Decennial Index of the Journal of the Society of Chemical Industry. Vols. XV to XXIV, 1896—1905. Part I, Index of Authors' Names. Compiled by *F. W.* **Renaut.** pp. 442. London 1907. (*Reference.*) From the Council.

Victoria. *Department of Agriculture.* Report . . . for the years 1905—07. pp. ix + 206. ill. Melbourne 1907. (*Recd.* 21/3/08.) From the Department.

II. *By Purchase.*

Kayser, *H.* Handbuch der Spectroscopie. Vol. 4. pp. 1248. Leipzig 1908. (*Recd.* 13/3/08.)

Zeitschrift für Chemie und Industrie der Kolloide. Edited by *Wolfgang* **Ostwald.** Year 2, etc. Dresden 1907 +. (*Reference.*)

III. *Pamphlets.*

Barrett, *W. H.* Wollaston: his life and work. (From the *J. Oxford University Junior Scientific Club,* 1907.)

Bihar Planters' Association. Report of the Indigo Research Station, Sirsiah (*under subsidy from the Government of Bengal*) for the year 1907—08. By *Cyril* **Bergtheil.** pp. 26. Calcutta 1908.

Dunlop, *Harry.* The testing of sperm oil and spermaceti. (From the *J. Soc. Chem. Ind.,* **27,** 1908.)

Friend, *J. Newton.* Ueber die Cupro-Verbindungen des Kohlenoxyds und die Ferro-Verbindungen des Stickoxyds. pp. 80. Würzburg 1908.

Lauder, *Alexander.* The variation in the composition of milk. Second annual report on the work at Rosslynlee, 1906—07. pp. 34. Edinburgh 1907.

New Zealand. *Department of Agriculture.* Chemistry division. Report, 1907. pp. 34. ill. Wellington 1907.

——— Bulletin No. 2. Wire-basket method of testing-soils. By *B. C.* **Aston.** pp. 11. ill. Wellington 1907.

Simon, *Theodor.* Ueber die Reduktion aromatischer Nitroverbindungen in saurer Lösung. pp. 76. Strassburg 1907.

At the next Ordinary Meeting, on **Thursday**, May **7th**, 1908, at **8.30** p.m., there will be a ballot for the election of Fellows, and the following papers will be communicated:

"Interaction of diazonium salts with mono- and di-hydric phenols and with naphthols." By K. J. P. Orton and R. W. Everatt.

"Condensation of benzoin with methyl alcohol." By J. C. Irvine and D. McNicoll.

"Mutual solubility of α-methylpiperidine and water." By O. Flaschner and B. MacEwen.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

The following Candidates have been proposed for election. A ballot will be held on Thursday, May 7th, 1908.

Allmand, Arthur John,
Central Laboratories, Widnes.
Chemist. Honours Graduate in Chemistry of the University of Liverpool; at present Research Chemist in the United Alkali Company, and Lecturer in Chemistry at Widnes Technical Schools.

F. G. Donnan. E. C. Weissmüller.
H. Bassett, jun. H. A. Auden.
Arthur Carey.

Baker, William Henry Benson,
Frognal Dene, Hampstead, N.W.
Student, Lincoln's Inn. B.A. Oxford; Honours in Final Chemistry School, 1906.

J. E. Marsh. W. W. Fisher.
T. V. Barker. A. Angel.
A. F. Walden.

Bowen, Josiah Leonard,
8, West Field, Lightcliffe, near Halifax.
Analytical Chemist. Studied Metallurgy and Analysis of Steel under tuition, and in the Laboratory, of F. J. Merrils, F.C.S., Sheffield. Studied Analytical Chemistry for five years under the tuition, and in the Laboratory, of F. W. Richardson, F.I.C., County Analyst to W.R.C.C., Yorkshire. Since April 1st, 1907, Research Chemist to

Messrs. Richardson and Jaffé, Analytical Chemists, Bradford. Researches upon "The Estimation of Adulterants in Turpentine." Co-author with F. W. Richardson, F.I.C., of a Paper "Determination of Mineral Acids in Vinegar" (*J. Soc. Chem. Ind.*, **XXV.**, 17, 15/9/06).

A. Jaffé. Walter M. Gardner.
Fredk. J. Merrils. B. North.
F. W. Richardson. *Walter Leach.*

Coverdale, Arthur Edward,

68, Broad Street, Worcester.

Pharmaceutical Chemist. Studied Chemistry under Dr. John Muter, F.I.C., F.C.S.; passed the minor and major examinations of the Pharmaceutical Society of Great Britain; conducts Analyses, and desires to keep in touch with the progress of chemistry and research.

John Muter. W. L. Howie.
A. H. M. Muter. *Thomas Tyrer.*
F. H. Alcock. *David Howard.*
Peter MacEwan.

Findley, Albert Edward,

1, Welford Road, Handsworth, Birmingham.

Demonstrator in Chemistry at Bradford Technical College. B.Sc. (Birmingham), Chemistry (principal subject) and Physics.

Percy F. Frankland. Thos. J. Murray.
Hamilton McCombie. C. K. Tinkler.
Alex. Findlay. Walter M. Gardner.
Barker North.

Gilling, Charles,

30, Carnarvon Road, Barnet.

Chemist. Pharmaceutical Chemist. Redwood Research Scholar of Pharmaceutical Society.

Arthur W. Crossley. J. Stuart Hills.
Chas. Horne Warner. M. Carteighe.
Walter Hills.

Green, Leonard Clifford,

Wienholt Street, Torwood, Brisbane, Queensland.

Lecturer in Chemistry at the Brisbane Technical College. Sydney University Senior Examination in Chemistry. Lecturer in Chemistry and Metallurgy, Brisbane Technical College. Analytical Chemist (professionally). Final 3rd Year Metallurgy B.E. degree, Sydney University, 1901.

J. C. Brünnich, F.I.C. P. W. Jones, A.I.C.
J. Brownlie Henderson, F.I.C. Hardolph Wasteneys.
A. B. Chater.

Hall, William,

Inglewhite, Manchester Road, Bolton.

Science Master. B.Sc. (Victoria University of Manchester); Chemistry was one of final subjects. Have taught the subject in Secondary Schools since 1897.

W. H. Perkin. Alfred Holt, jun.
J. F. Thorpe. G. H. Bailey.
Norman Smith.

Holden, George Edward,

23, Durnford St., Middleton, Manchester.

Works Chemist. Honours in Chemistry; Lecturer on Dyeing, Middleton. Diploma of the Municipal School of Technology. 1st class Hons., full Technological certificates, for Dyeing, Bleaching, Printing, Oils and Fats, 1st Coal Tar, &c.

W. J. Pope. L. G. Radcliffe.
Jas. Grant. John Allan.
Stanley J. Peachey. F. S. Sinnatt.

Hornby, Percy Holme,

111, Nine Elms Lane, S.W.

Chemist to the Brentford Gas Co. Studied Chemistry under Mr. J. Hornby, F.I.C. Held the position of chemist to the Ilford Gas Co. for 3½ years. At present occupy the position of chemist to the Brentford Gas Co. Have devoted considerable time to original research, more particularly cyanides.

S. G. Rawson. W. J. Atkinson Butterfield.
J. Wilson. *Charles A. Keane.*
Bertram Blount.

Kohn, Hugo Stefan, Ph.D.,

3A, Hythe Road, Willesden Junction.

Works Manager. I studied Chemistry at the Universities of Munich and Berlin; at the latter I took my degree in 1902 by the investigation, "Beitrag zum Abbau von Zuckern; Darstellung der *l*-Threose und der Methyltetrose," as published in the *Berichte d.dtsch. chem. Gesellsch.*

R. Lessing. E. P. Andreae.
Otto Oberländer. *R. W. Sindall.*
A. Hann.

Lynch, Gerald Roche,

160, Holland Park Avenue, W.

Advanced student at the Central Technical College, South

Kensington. Joint author with N. H. Alcock of "The Relation between the Physical and Chemical Properties of the Nerves. Part I," from *Journal of Physiology*.

Henry E. Armstrong. George Senter.
William A. Davis. W. Robertson.
Gerald T. Moody. Robert J. Caldwell.

Mansfield, Herbert,

70, Stapleton Hall Rd., Stroud Green, N.

Analytical Chemist. Bachelor of Science of the London University, with Honours in Chemistry. Associate of the Institute of Chemistry. Assistant to Dr. Frank L. Teed. Deputy Gas Examiner to the London County Council. At present engaged on research at the East London College.

Frank L. Teed. Clarence Smith.
J. T. Hewitt. J. J. Fox.
Horace Finnemore.

Maywald, Frederick J.,

1028, 72nd Street, Brooklyn, N.Y., U.S.A.

Consulting and Research Chemist. I have been associated with the late Dr. Peter T. Austen in the above lines of work for 14 years, and have worked out various processes which have since been patented.

T. Lynton Briggs. J. Livingston R. Morgan.
Marston T. Bogert. C. F. Chandler.
William S. Myers.

Meade, Alwyne Harcourt,

Cedar House, St. Neots, Huntingdonshire.

Gas Engineer. Studied chemistry for 4 years at Oundle College, Northants. Oxford and Cambridge Certificate (first class pass in chemistry). City and Guilds of London Institute—first class honours pass in Gas Engineering. Assistant to Commercial Gas Company London.

Thos. R. Duggan. *F. Napier Sutton.*
H. F. Hills. *W. J. Atkinson Butterfield.*
Harold G. Colman. *Vivian B. Lewes.*
H. O. Hale. *Samuel Rideal.*
H. Leicester Greville. *Kenneth M. Chance.*

Melling, Samuel Ernest,

The Cliff, Higher Broughton, Manchester.

Analytical chemist. Fellow of the Institute of Chemistry. Student

at Owens College, Manchester, 1894–7. Five years with the late Mr. A. H. Allen, and for the past five years in partnership with Mr. J. Carter Bell, County and Public Analyst. Public Analyst for the County Borough of Wigan. Deputy Agricultural Analyst for the County of Chester, &c.

J. Carter Bell. — Alf. C. Chapman.
Otto Hehner. — Arthur E. Ekins.
Edward Bevan. — G. E. Scott-Smith.

Neech, Herbert Richard,
20, Colegrave Street, Lincoln.

Analytical Chemist and Chemical Engineer. Studied Chemistry (inorganic and organic) for five years at the Lincoln School of Science. Hold South Kensington First Class Advanced Certificates for Chemistry (Theoretical and Practical) and other Sciences, also City and Guilds Certificate for Electrical Engineering. Have acted as Assistant Chemist to Messrs. Morris Brothers, Doncaster, for nine years. Occupied position of Chemist to Productos Quimicos de Huelva, S.A., for eighteen months. At present Consulting Chemist in Lincoln. Am interested in all branches of Chemistry, and am desirous of obtaining the Society's Journals and publications.

John Shields. — J. Hope Belcher.
Clarence H. Creasey. — Wm. T. Gent.
Walter Birkett.

Phillips, Thomas Richards,
Stanhope House, Abergavenny.

Inspector of Inland Revenue. First class Organic and Inorganic Chemistry, Royal College of Science, South Kensington. Three years Assistant in the Government Laboratory, London. Interested in Chemical Science.

E. Grant Hooper. — E. Jones.
C. Proctor. — J. Woodward.
J. H. Robbins. — *Geo. Stubbs.*
J. J. Fox.

Richards, Francis Edward,
County Secondary School, Redruth.

Science Master at the County School, Redruth. Joint Author, with Dr. G. T. Morgan, of a paper on "Azo-colouring matters derived from *as*-Tetrahydro-*α*-naphthylamine" (*Journ. Soc. Chem. Ind.*, June 30, 1905). Chemistry teacher as above. A.R.C.S. (London) in Chemistry and B.Sc. (Lond.) Hons. in Chemistry.

William A. Tilden. — James C. Philip.
M. O. Forster. — Chapman Jones.
G. T. Morgan.

Watkins, Edwin John,

10, Montpelier Road, Queens Road, Peckham, S.E.

Analyst and Technical Chemist; engaged in the manufacture of Cereal and Malted Food Products; at present with Mellin's Food Ltd., Peckham, London, S.E. Student—Chemistry, Physics—during five years at St. Thomas Charterhouse Science Schools; also three years at Borough Polytechnic Laboratories. Bacteriology, two sessions, King's College. Assistant and Demonstrator to J. J. Pilley, Ph.D. Member of Society of Chemical Industry. Author of "Investigations Touching the Cause of Rope Disease in Flour and Bread" (*Journ. Soc. Chem. Ind.*, 1906, **8**, 350—357). Author of articles on Chemistry in *Modern Baker, Confectioner, &c.*, London, 1907. Also many articles on chemistry in bakery trade journals.

John J. Pilley. — John B. Coppock.
F. Mollwo Perkin. — Alfred Gordon Salamon.
D. S. Kemp. — Julian L. Baker.

Wheatley, William,

21, Bairstow Street, Preston.

Science Master, Preston Grammar School. B.A., 2nd Class Honours, Chemistry, Oxford, 1907.

W. W. Fisher. — Allan F. Walden.
J. E. Marsh. — A. Angel.
John Watts. — N. V. Sidgwick.

The following Certificates have been authorised by the Council under Bye-Law I (3):

Dutt, Bidhu Bhushan,

Calcutta.

Lecturer in Chemistry, Presidency College, Calcutta. M.A. in Chemistry of Calcutta University. Author of a Paper on "Reactions at Low Temperatures," published in the Proceedings of the Asiatic Society of Bengal. Assistant in the Chemical Department at Presidency College, Calcutta, during the last three years.

J. A. Cunningham. — P. C. Rây.
E. R. Watson.

Ganguli, Atul Chandra,

Cuttack, Orissa, India.

Professor of Chemistry, Ravenshaw College, Cuttack. B.A. of Calcutta University, with Honours in Chemistry and Physics. Joint author (with Prof. P. C. Rây, D.Sc.) of several papers published in

the Transactions of the Chemical Society. For many years Assistant in the Chemical Department, Presidency College, Calcutta.

J. A. Cunningham. P. C. Rây.

E. R. Watson.

Hinds, Cyril Arden,

724, Russell Street, Bristol, Tenn., U.S.A.

Chief Chemist, Bristol Barium and Zinc Works, John T. Williams and Son, props. Student in Science Department at Harrison College, Barbados, for 5½ years, during which time chemistry, theoretical and practical, was one of the subjects studied; junior assistant for 10 months at Govt. Laby., Barbados. At present as above *vide* occupation.

J. P. d'Albuquerque. John R. Bovell.

E. Gillman.

Horrobin, Arthur,

Ajmer, Rajputana, India.

Analytical Chemist. Five years as Assistant in Laboratory of the "Lancashire and Yorkshire Railway Company"; two years in charge of Electrochemical department of "The Chloride Electrical Storage Company's" works, Lancashire; four and a-half years Chief Assistant Chemist "East Indian Railway Company," and now Chemist to "Bombay, Baroda, and Central India Railway Company"; I am desirous of obtaining Journal and keeping in touch with the advancement of chemical science.

Chas. J. P. Fuller.

Neogi, Panchānan,

Rajshahi, Eastern Bengal and Assam.

Professor of Chemistry, Rajshahi College. M.A. in Chemistry, Calcutta University, and Premchand Roychand Research Scholar, 1906. Author of Papers published in the Transactions of the Chemical Society and the Proceedings of the Asiatic Society of Bengal.

J. A. Cunningham. P. C. Rây.

E. R. Watson.

Seelhorst, William,

Chemist to the Eastern Smelting Co., Ltd., Penang, Straits Settlements. Previously for eight years senior Laboratory Assistant in the Government Laboratory, Singapore, S.S., under Mr. Percival J. Burgess, M.A., F.C.S., and Dr. Frankland Dent, M.Sc., Ph.D., F.I.C., J.P., and Mr. John R. Brooke, F.I.C., F.C.S., J.P. Reasons the applicant desires to become a Fellow: To keep abreast of current chemical literature, of which there is little in the Colony.

John R. Brooke.

RICHARD CLAY AND SONS, LIMITED, BREAD ST. HILL, E.C., AND BUNGAY, SUFFOLK.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 24. No. 341

Thursday, May 7th, 1908, at 8.30 p.m., Professor E. DIVERS, F.R.S., in the Chair.

Mr. K. S. Caldwell was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. :

Charles Duncan Cooper, 776, Oxford Road, Reading.
John Robert Cowburn, Belmont Villa, Birkbeck Grove, Acton, W.
Kaufman George Falk, B.Sc., Ph.D., 1070, Madison Avenue, New York City.
Norman Holland, 4907, Sherbrooke Street W., Montreal.
James Kirkman King, B.A., 55, Brewery Road, Plumstead.
Lionel Gordon Larmuth, Grove House, Cheadle Hulme, Manchester.
Henry Robert Lyell, Redcott, Dacres Road, Sydenham, S.E.
Haradhan Ray, M.A., 4, Jhamapooker Lane, Calcutta.
William Readwin, 6, Kirkfield Terrace, Morley, near Leeds.
Alexander Mackintosh Stewart, Penang, Straits Settlements.
Herbert Horace Ward, University College of Wales, Aberystwyth.
Charles Harold Wright, B.A., Government Laboratory, Port of Spain, Trinidad.
Charles Robert Young, B.Sc., 11, Low Pavement, Nottingham.

A Ballot for the election of Fellows was held, and the following were subsequently declared duly elected:

Arthur John Allmand, M.Sc.
William Henry Benson Baker, B.A.
Josiah Leonard Bowen.
Arthur Edward Coverdale.
Bidhu Bhushan Dutt, M.A.
Albert Edward Findley, B.Sc.
Atul Chandra Gañguli, B.A.
Charles Gilling.
Leonard Clifford Green, B.E.
William Hall, B.Sc.
Cyril Arden Hinds.
George Edward Holden.
Percy Hulme Hornby.
Arthur Horrobin.
Hugo Stefan Kohn, Ph.D.
Gerald Roche Lynch.
Herbert Mansfield, B.Sc.
Frederick J. Maywald.
Alwyne Harcourt Meade.
Samuel Ernest Melling.
Herbert Richard Neech.
Pañchānan Neogi, M.A.
Thomas Richards Phillips.
Francis Edward Richards, B.Sc.
William Seelhorst.
Edwin John Watkins.
William Wheatley, B.A.

Of the following papers, those marked * were read:—

***89. "The refraction and dispersion of triazo-compounds." By James Charles Philip.**

The molecular refraction and dispersion of a number of compounds containing the triazo-group have been determined. A study of these constants shows that the contribution which the N_3-group normally makes to the molecular refraction is 8·91 units, almost the same value as the atomic refraction of bromine. The contribution which the N_3-group normally makes to the molecular dispersion is 0·36—0·37, whilst the atomic dispersion of bromine is 0·35. In certain compounds, namely, ethyl triazoformate, phenylazoimide, and α-naphthylazoimide, the refractive and dispersive powers of the N_3-group are considerably above the normal values. Such "optical exaltation" (Brühl, *Ber.*, 1907, **40**, 878) is generally associated with the existence in the molecule of contiguous unsaturated groups, and it will be seen that in each of the three triazo-compounds mentioned the N_3-group is in conjugation with an unsaturated group. The bearing of these results on the formulation of the N_3-group was discussed.

***90. "The dissociation constants of triazoacetic and α-triazopropionic acids." By James Charles Philip.**

The conductivity of solutions of these acids has been determined in the usual way. The values obtained for the expression $k = \alpha^2/(1-\alpha)v$ diminish to some extent as the dilution increases, but are sufficiently constant to indicate the strengths of the two acids. The value of k

for triazoacetic acid is 0·00090—0·00100, whilst that for α-triazopropionic acid is slightly less, about 0·00086. These values show that the introduction of the N_3-group into the molecule of acetic or propionic acid increases the strength of the acid nearly as much as the introduction of a bromine atom. It is noteworthy, also, that the conductivity of the triazoacetate ion is the same as that of the monobromoacetate ion.

Discussion.

Mr. H. Stanley Redgrove called attention to a paper (*Chem. News*, 1907, **95**, 193) in which he proved that in general the alleged atomic constants employed in calculating additive physicochemical constants (such as Brühl's mol.-refractivity constants) were incorrect and, in the present state of our knowledge, unobtainable.

This was due to the fact that the specific influence due to certain linkings (for example, the "ethane" carbon linking) is neglected. In the paper quoted, he had outlined a general method of calculation by means of the so-called "fundamental constants," whereby the above assumption is avoided, and was applying it with success to the calculation of thermal constants.

Allowing for this, Brühl's hydrogen constant was really the value of the hydrogen atom plus the C·H link decreased by half the value of a C·C link, and his carbon constant the value of the carbon atom increased by twice the value of a C·C link, &c., so that the triazo-constant would be the value of the triazo-group plus the link joining it to carbon decreased by half the value of a C·C link.

***91. "The fermentation of mannose and lævulose by yeast-juice." (Preliminary note.) By Arthur Harden and William John Young.**

1. Mannose is fermented by yeast-juice at almost the same rate as dextrose.

2. Lævulose is fermented somewhat more rapidly than dextrose, the rate varying with different samples of yeast-juice from 1·2 to 1·8, compared with that of dextrose = 1.

3. Mannose and lævulose behave qualitatively towards phosphates in the presence of yeast-juice in a similar manner to dextrose.

(*a*) When a phosphate is added to a fermenting mixture containing either of these sugars, the phosphate is converted into a hexosephosphate not precipitable by magnesia mixture; the rate of fermentation is temporarily greatly accelerated, and during this period an extra amount of carbon dioxide is evolved, equivalent to the phosphate added:

the rate then rapidly diminishes, and falls to a value equal to, or slightly greater than, that which it had before the addition of the phosphate.

The fermentation of mannose and lævulose by yeast-juice therefore probably proceeds according to the same two equations as have been previously proposed by the authors for dextrose:

(1) $2C_6H_{12}O_6 + 2R_2'HPO_4 = 2CO_2 + 2C_2H_6O + C_6H_{10}O_4(PO_4R_2')_2 + 2H_2O$.

(2) $C_6H_{10}O_4(PO_4R_2')_2 + 2H_2O = C_6H_{12}O_6 + 2R_2'HPO_4$.

(*b*) As in the case of dextrose, an optimum concentration of phosphate exists, which produces a maximum rate of fermentation. Increase of concentration beyond this maximum diminishes the rate of fermentation produced, until, with a sufficiently great concentration of phosphate, the rate is less than that of the juice in the absence of added phosphate.

4. The quantitative relations of mannose to phosphates are practically the same as those of dextrose.

The maximum rate produced by lævulose, on the other hand, is much greater than (about double) that produced by dextrose or mannose. The accelerated fermentation of lævulose in presence of phosphate, moreover, is much less readily inhibited than that of dextrose or mannose by the further addition of phosphate, the difference in this respect being very marked.

5. Lævulose possesses the property of inducing rapid fermentation in a mixture of dextrose or mannose with yeast-juice, in which fermentation has been inhibited by a large excess of phosphate and in which the concentration of free phosphate is maintained constant throughout the experiment. Dextrose and mannose have not a similar power. The amount of lævulose required to produce this effect is comparatively small. Thus, for a mixture of 15 c.c. of yeast-juice with 15 c.c. of a 0·6 molar solution of potassium phosphate and 2 grams of dextrose fermenting at the rate of 0·7 c.c. per five minutes, the addition of 0·05 gram of lævulose was found to be sufficient, the maximum rate produced being 17 c.c. per five minutes. The effect is not due to the preferential fermentation of the lævulose, as the amount of gas evolved far exceeds that which could be derived from this source.

The nature of this reaction is still under investigation.

Discussion.

Mr. Grant Hooper asked if Dr. Harden had examined the effect of phosphates on yeast as distinct from yeast-juice. In view of the fact that phosphates had been often used in the so-called "Yeast Foods" offered to or employed by brewers, it would be interesting to know whether the authors had observed whether the

addition of phosphate to normal fermentations with yeast had the same effect as when added to yeast-juice.

Dr. HARDEN, in his reply, said that Slator had recently observed that the fermentation caused by yeast was not accelerated by phosphate.

***92. "The constituents of olive leaves." By Frederick Belding Power and Frank Tutin.**

Air-dried olive leaves were percolated with hot alcohol, when they gave about 30 per cent. of their weight of extracted material. This alcoholic extract yielded, besides some amorphous matter, the following products:

(1) A new *monocarboxylic acid*, $C_{22}H_{45}\cdot CO_2H$ (m. p. 68—69°); (2) a small amount of a mixture of fatty acids, containing oleic acid; (3) hentriacontane, $C_{31}H_{64}$ (m. p. 68—69°); (4) pentatriacontane, $C_{35}H_{72}$ (m. p. 74·5°); (5) *oleasterol*, $C_{20}H_{34}O$ (m. p. 174°), a new, crystalline alcohol related to the phytosterols; (6) a new, crystalline alcohol, *olestranol*, $C_{25}H_{42}O_2$ (m. p. 217—218°), which appears to be a hydroxyphytosterol; (7) *homo-olestranol*, $C_{27}H_{46}O_2$ (m. p. 210°; $[\alpha]_D$ +71°), a compound similar to olestranol; (8) an amount of *d*-mannitol equivalent to about 3·4 per cent. of the weight of air-dried leaves; (9) a considerable amount of a sugar which yields *d*-phenylglucosazone; (10) a trace of an essential oil; (11) *oleanol*, $C_{31}H_{48}O(OH)_2,H_2O$ (m. p. 303—304°; $[\alpha]_D$ +78·3°), a new, crystalline substance in an amount equivalent to nearly 3·4 per cent. of the weight of air-dried leaves. This compound contains one alcoholic and one phenolic hydroxyl group. *Monomethyloleanol*, $C_{31}H_{48}O(OH)\cdot O\cdot CH_3$, melts at 194—195°, and on acetylation yields *acetylmethyloleanol*, $C_{31}H_{48}O_2(O\cdot CH_3)\cdot CO\cdot CH_3$ (m. p. 215·5°). *Diacetyloleanol*, $C_{31}H_{48}O_3(CO\cdot CH_3)_2$, when heated to about 210°, gives a *substance*, $C_{31}H_{48}O_3$, which does not fuse at 310°. *Monoacetyloleanol*, $C_{31}H_{48}O_2(OH)\cdot CO\cdot CH_3$, melts at 258°.

***93. "The constituents of olive bark." By Frederick Belding Power and Frank Tutin.**

Air-dried olive bark, on percolation with hot alcohol, yielded about 30 per cent. of its weight of extracted material. From this alcoholic extract the following crystalline compounds were obtained, together with some amorphous products.

(1) A new *monocarboxylic acid*, $C_{34}H_{67}\cdot CO_2H$ (m. p. 69—70°), which yields an *ethyl* ester melting at 63°; (2) a new *monocarboxylic acid*, $C_{24}H_{45}\cdot CO_2H$ (m. p. 79°), the *ethyl* ester of which melts at 66·5°;

(3) a new *monocarboxylic acid*, $C_{34}H_{69}\cdot CO_2H$ (m. p. 92°), which yields an *ethyl* ester melting at 87°; (4) a new *monocarboxylic acid*, $C_{29}H_{57}\cdot CO_2H$ (m. p. 84°), the *ethyl* ester of which melts at 75°; (5) a *substance*, probably a *tertiary alcohol*, $C_{35}H_{68}O$ (m. p. 70°); (6) pentatriacontane, $C_{35}H_{72}$ (m. p. 74—75°); (7) a phytosterol, $C_{27}H_{46}O$ (m. p. 136°; $[\alpha]_D - 35{\cdot}2°$), which yields an acetyl derivative melting at 119·5°; (8) a *substance*, $C_{23}H_{38}O_2(OH)_2$ (m. p. 285—290°), which yields an *acetyl* derivative melting at 160°, and is identical with *ipuranol*, a compound recently isolated by Power and Rogerson from *Ipomoea purpurea*; (9) a new phenolic substance, *olenitol*, $C_{14}H_{10}O_6$ (m. p. 265°), dilute solutions of which show a blue fluorescence. *Acetylolenitol* melts at 130°; (10) *d*-mannitol, in an amount equivalent to 1·9 per cent. of the weight of air-dried bark; (11) a sugar which yields *d*-phenylglucosazone.

94. "The reaction of diazonium salts with mono- and di-hydric phenols and with naphthols." By Kennedy Joseph Previté Orton and Reginald William Everatt.

The behaviour of a series of typical diazonium salts, mainly hydrogen sulphates, with phenols in alcohol, water, and other solvents has been examined. All diazonium salts couple quantitatively with α- and β-naphthols in alcoholic media, but under similar conditions these salts do not combine with monohydric phenols.

The dihydric phenols, resorcinol and orcinol, resemble the naphthols, reacting readily with all diazonium salts in alcoholic solution. In aqueous solution, on the other hand, only those diazonium salts with a preponderance of negative substituents (halogen atoms) in the benzene nucleus couple completely with the two dihydric phenols. In other cases, unless the acidity has been reduced by sodium acetate, the coupling is either partial or absent, according to the character of the substituents of the benzene nucleus.

It is a remarkable fact that those diazonium salts possessing halogen atoms in the positions 2, 4, and 6 with respect to the diazo-group (for example, *s*-tribromodiazobenzene) will react rapidly and quantitatively with resorcinol and orcinol in solution in 50 per cent. sulphuric acid.

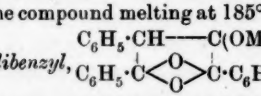
Diazonium salts are converted by quinol in aqueous or alcoholic solution into the corresponding hydrocarbon, thus:

$$Ar\cdot N_2HSO_4 + OH\cdot C_6H_4\cdot OH = ArH + N_2 + H_2SO_4 + O{:}C_6H_4{:}O.$$

With catechol, either coupling or a similar reaction to that with quinol takes place, according to the nature of the substituents in the benzene nucleus of the diazonium salt.

A number of azoresorcinols and azo-orcinols were described.

95. "The condensation of benzoin with methyl alcohol." By James Colquhoun Irvine and David McNicoll.

It has already been noticed (*Trans.*, 1907, **91**, 1384) that during the methylation of benzoin by Fischer's method two by-products (m. p. 185° and 285°) are formed in varying quantity, according to the conditions of the reaction. As one of the compounds appeared to be produced by the condensation of benzoin methyl ether, the constitution and mode of formation of both substances have been further examined. The results show that the compounds are tetraphenylfuran derivatives, and the formulæ previously suggested are therefore no longer tenable. Both substances give the same triacetyl derivative when treated with acetic anhydride and sulphuric acid in the cold, and this in turn, when warmed with the reagent, is converted into acicular dibenzoylstilbene. The compound of lower melting point is converted into the other by the action of methyl alcohol and hydrogen chloride, and both substances are formed when dibenzoylstilbene is subjected to a similar reaction. The compound melting at 185° is thus regarded as *aβ-dibenzoyl-α-methoxydibenzyl*,  , and the second compound (m. p. 285°) as 2-*hydroxy*-3 : 5-*dimethoxytetraphenyltetrahydrofuran*, conclusions which are supported by the action of hydrogen iodide on each. Apparently the formation of the compounds takes place during the methylation prior to the formation of benzoin methyl ether, and is doubtless owing to the dehydration of the benzoin to form dibenzoylstilbene, which then unites with two molecules of methyl alcohol in two successive stages.

The occurrence of similar side reactions has also been noticed in the methylation of anisoin.

96. "The mutual solubility of 2-methylpiperidine and water." By Otto Flaschner and Basil MacEwen.

The influence of constitution on one of the two critical solution temperatures of mutually soluble liquids was discussed. Nitrogen and oxygen atoms increase the mutual solubility when one of the liquids is water, whilst carbon and hydrogen atoms decrease it. In order to ascertain the influence of the position of a substituted group in a cyclic compound, the mutual solubility of 2-methylpiperidine and water has been examined. This is represented by a closed curve. The lower critical solution temperature is 79°, and the higher one 227°.

97. "The melting points of the anilides, *p*-toluidides, and *α*-naphthalides of the normal fatty acids." By Philip Wilfred Robertson.

The melting points of the fatty amides do not exhibit any regularity even if the odd or even members are considered separately. The anilides also show the same exceptional behaviour, and, in order to obtain a more definite insight into the relationship between melting point and number of carbon atoms in a homologous series, the missing members have been prepared as well as a complete series of the *p*-toluidides. The irregularities in these two series seem to tend always in the reverse direction to those observed in the case of the amides. On taking the mean melting points of the amides and anilides, and of the amides and *p*-toluidides, the disturbing factor, which is considered to be a function of the lack of symmetry of the molecule, is to a great extent eliminated, as regular series of numbers are obtained.

In the fatty *α*-naphthalides, where the substituent group is heavier, irregularities tend to disappear: the melting points of the even members descend to a minimum at the eighth member and then rise gradually, whilst there is a corresponding minimum in the case of the odd series at the ninth member.

98. "The absorption spectrum of camphor." By Walter Noel Hartley.

The absorption spectrum of solutions of camphor was examined in 1881 (Hartley, *Trans.*, **39**, 153) and compared with the spectra of benzene and its derivatives. There was a difficulty in obtaining it free from impurities showing absorption bands. Camphor sublimed in sunlight and condensed in large crystals, showed no band, and was remarkably diactinic. In view of more recent work, it was decided to re-examine the spectrum of camphor very carefully. The result has been to show that when solutions of ten times the concentration usually employed in such experiments are examined, a band occurs in the spectrum, due to the occurrence of the CO and CH_2 groups in the molecule. This is in general agreement with the work of Baly, Marsden, and Stewart (*Trans.*, 1906, **89**, 979), but otherwise the substance is remarkably diactinic.

99. "The viscosity of solutions." By Charles Edward Fawsitt.

In continuation of previous work (*Zeitsch. physikal. Chem.*, 1904, 48, 585; *Electrochemist and Metallurgist*, 1904, 3, 664), a number of colloidal solutions and alcoholic solutions have been examined. In dilute solutions, the viscosity is, in general, a linear function of the concentration. If the viscosities of solutions of the substances in a homologous series are compared, the relation of viscosity to composition appears to be largely additive.

100. "The action of fused potassium hydroxide and of hydrogen peroxide on cholesterol." (Preliminary note.) By Robert Howson Pickard and Joseph Yates.

Cholesterol is slowly decomposed by prolonged fusion with potassium hydroxide. From the products of the decomposition, small quantities of two crystalline acids have been isolated. The *acid*, $C_{26}H_{44}(OH)\cdot CO_2H$, melts at 241°, is optically active, and forms an *acetyl* derivative (m. p. 163°) and an *ethyl* ester (m. p. 62°). The *acid*, $C_{24}H_{42}(CO_2H)_2$, melts at 190°, and forms an amorphous *silver* salt.

Cholesterol or its acetate is also rapidly attacked by hydrogen peroxide, which is employed to the best advantage under the conditions described by W. H. Perkin, jun. (*Proc.*, 1907, **23**, 166). The main product is a neutral *substance*, $C_{27}H_{46}$(or $_{48}$)O_3, m. p. 239°, which is probably isomeric with dehydrocholestantriol (Windaus, *Ber.*, 1907, **40**, 257). The *monoacetate* melts at 212°, the *diacetate* at 165°, and the *dipropionate* at 172°. It may be oxidised to a *keto-alcohol*, $C_{27}H_{44}O_3$ (m. p. 232°), which forms a *monoacetate*, m. p. 233°, and a *phenylhydrazone*, m. p. 164°. The substances melting at 239° and 232° contain the hydroxyl group of cholesterol, and are readily oxidised to the diketo-alcohol ("oxycholestendiol") described by Mauthner and Suida (*Monatsh.*, 1896, **17**, 590). Dicholesteryl ether behaves in an analogous manner with hydrogen peroxide, forming a neutral *substance*, $(C_{27}H_{45}O_2)_2O$ (?), which melts at 192° and forms a *diacetate*, m. p. 143°. The formation of these substances appears to confirm the deductions of Windaus (see summary in *Arch. Pharm.*, 1908, **246**, 117) as to the relation between the constitution of cholesterol and that of some of the products of its oxidation by ermanganic and chromic acids.

101. "The volumetric estimation of silver." By William Robert Lang and J. C. Woodhouse.

The apparatus employed for the estimation of sulphates and salts of barium (*Trans.*, 1907, **91**, 1370) was found unsuitable for the determination of silver, owing to the slowness with which the milky solution in the thin tube cleared. Some filtering medium appeared necessary, so, after several unsuccessful attempts with glass-wool and with asbestos, clean sand was used, held in position by a glass-wool plug in a curved tube. The packed sand filter necessitated the use of a filter-pump for washing, and was found a great convenience. Experiments were made with solutions containing a known amount (0·5 gram) of silver, to which an excess of $N/10$ sodium chloride was added and the excess titrated with $N/10$ silver nitrate. Each titration occupied about half an hour, and the mean error of six determinations was 0·286 per cent. On using 1 gram of silver, 100 c.c. of $N/10$ sodium chloride, and titrating back with $N/100$ silver nitrate, the error was reduced to 0·198 per cent. The effect of free nitric acid in varying amounts on the estimation was also tried and found to reduce the error still further, as low as 0·063 per cent The method and apparatus were then employed to determine silver in bullion under the same conditions as obtained in the Gay-Lussac method, namely, 1 gram of silver in nitric acid, 100 c.c. of $N/10$ sodium chloride, and finishing with $N/100$ silver nitrate. The result of seven estimations done in this way, each occupying about half an hour, gave a mean error of 0·067 per cent. It seems reasonable to hope that this apparatus may prove of use to those requiring a rapid and accurate method of estimating silver.

102. "A criticism of Werner's theory, and the constitution of complex salts." By John Albert Newton Friend.

The author pointed out the disadvantages of Werner's theory, as applied to simple and complex salts, and suggested new structural formulæ which are free from these objections.

103. "The action between potassium sulphite and potassium pentathionate." By Edward Divers.

Debus published, in 1888, a paper on the polythionic acids (*Trans.*, **53**, 278), which is still a classic on the subject, but can remain so only so long as later researches leave its accuracy in all essentials untouched. It is therefore important to point out that the accuracy of Debus's investigation of the action between a sulphite and a penta-

thionate is not affected by Colefax's quite recent work (*Trans.*, 1908, 93, 798), as it would appear to be from pp. 803—804 of that author's paper. Debus is in agreement with Colefax, but his work is more comprehensive than Colefax's and with a wider object in view.

Colefax has found that potassium sulphite in solution is, nearly all, rapidly converted by potassium pentathionate into the thiosulphate, whilst Debus has stated (*loc. cit.*, p. 344) that "potassic sulphite and potassic pentathionate form potassic thiosulphate and potassic trithionate." The latter author's experimental proof of this is given on p. 332, but in an irregular form, for, instead of using potassium sulphite, he dissolved the potassium pentathionate in a concentrated solution of sulphur dioxide and then added barium carbonate. He gives two chemical equations in explanation of this procedure, which are equivalent to $K_2S_5O_6 + 2K_2SO_3 = K_2S_3O_6 + 2K_2S_2O_3$, an equation indicating a 50 per cent. fall in iodine titration-value, in accordance with Colefax's observations. By using barium carbonate, Debus accomplished an easy separation of the products, obtaining the thiosulphate as insoluble barium salt, and the trithionate as potassium salt, in crystals. Colefax worked throughout his investigations on molecular proportions of his salts, as was proper for the end he had in view, but the addition to the above equation of a second molecule of pentathionate is without effect on the action it expresses or on the iodine value. Working quantitatively, and with the actual salts, Colefax has made, it should be added, a real addition to our knowledge of the reaction.

Debus did experiment with potassium sulphite itself, converting it into thiosulphate by the pentathionate, but he employed solutions a hundred times stronger than those used by Colefax, with the result, not met with by the latter, that he also obtained much sulphur dioxide. His explanation of this evolution of sulphur dioxide is a suggestion of deep theoretical significance, if well founded, with apparently no other explanation possible in place of it. His experiment has no bearing on Colefax's investigation with highly dilute solutions, and Debus's explanation of it is certainly quite inapplicable to the results obtained in other ways, both by himself and by Colefax, as the latter has rightly pointed out in connexion with his own work.

104. "Note on phenolic thetines and their action with benzoyl chloride." By Edward de Barry Barnett and Samuel Smiles.

When phenol and phenetole *p*-sulphoxide are dissolved in concentrated sulphuric acid, *phenoxydiphenetylsulphonium sulphate* is formed. The *platinichloride* of the base is an orange-brown powder melting at

123—125°. The condensation of diphenyl sulphoxide with phenol does not take place in cold sulphuric acid, but it may readily be effected by warming with phosphoric oxide. *Phenoxydiphenylsulphonium platinichloride* occurs in orange crystals, which rapidly decompose at about 210°. The salts of these bases are colourless, viscous oils. On treatment with aqueous alkali hydroxide, they yield the phenolic thetines. These are unstable, yellow oils, which are soluble in water or chloroform and insoluble in concentrated aqueous alkali hydroxide. They are formed (by elimination of alkali salt) from the sodium salt of the sulphonium base,

$$(C_6H_5)_2(C_6H_4\cdot ONa)SCl = NaCl + (C_6H_5)_2{:}\underset{|}{S}\cdot C_6H_4\cdot \underset{|}{O}.$$

With benzoyl chloride in aqueous alkaline solution, the phenolic thetines yield benzoic anhydride, and in this respect they resemble certain tertiary nitrogen bases, for example, pyridine (Minunni, *Gazzetta*, 1892, **22**, 215). With hydrochloric acid they furnish the chlorides of the corresponding sulphonium bases.

105. "The relation between dielectric constant and chemical constitution. Part I. Stereoisomeric compounds." By Alfred Walter Stewart.

The author has examined active and racemic compounds and also geometrical isomerides, and finds that the influence of the spacial arrangement of atoms on the dielectric constants of isomeric substances is not clearly marked. A difference in electric absorption was noticed in one case, the active isomeride having a stronger absorptive power than the racemic form.

106. "An apparatus for determining the specific inductive capacity of organic liquids." By Alfred Walter Stewart.

In this apparatus, Hertzian waves are generated and conducted along a secondary circuit in the usual manner. The secondary circuit is led through a vertical graduated tube, and an adjustable bridge between the wires of the circuit is obtained by moving mercury up and down within the tube. The apparatus is calibrated in the usual way, by means of liquids of known specific inductive capacity. The chief advantages over the previous method (Drude, *Zeitsch. physikal. Chem.*, 1897, **23**, 267) lie in the regulation of temperature by jacketing the tube (which could not be done easily in the Drude apparatus), in the sharpness of contact between the mercury and the wires of the secondary circuit, and in the comparatively small quantity of substance required for the new apparatus. Reduced pressures can also be used.

107. "The influence of solvents on the rotation of optically active compounds. Part XII. Ethyl tartrate in aromatic halogen derivatives." By Thomas Stewart Patterson and David Paterson McDonald.

The rotation of ethyl tartrate has been examined in chlorobenzene, bromobenzene, iodobenzene, *p*-dichlorobenzene, and α-bromonaphthalene. The data were compared with others formerly obtained for benzene and for various aliphatic halogen derivatives. The relationship between rotation and molecular solution-volume in these solvents was discussed, as was also the influence of temperature change on the rotation of dilute solutions of ethyl tartrate in α-bromonaphthalene.

108. "A new test for silver." By Arnold William Gregory.

When a solution of a silver salt is added to a mixture of 20 c.c. of aqueous ammonium salicylate (20 grams of salicylic acid neutralised with ammonium hydroxide, a slight excess of the latter added, and the solution made up to 1 litre) and 20 c.c. of ammonium persulphate solution (50 grams in 1 litre), an intense brown colour is produced. By this reaction, 0·01 milligram of silver can be detected. As lead does not give this reaction, silver may be tested for in presence of this element; 1·1 milligram of silver may be detected in this manner in the presence of 0·2 gram of lead.

It was found that the brown substance formed in this reaction does not contain silver, and it is probable that the silver salt acts as a catalyst, since on boiling a solution of ammonium salicylate with ammonium persulphate a similar brown colour is produced.

109. "The spontaneous crystallisation of substances which form a continuous series of mixed crystals: mixtures of naphthalene and β-naphthol." By Henry Alexander Miers and Florence Isaac.

The object of this research was tc ascertain whether there are definite temperatures of spontaneous crystallisation in mixtures which yield a continuous series of mixed crystals.

By means of experiments on mixtures of naphthalene and β-naphthol of known composition contained in sealed tubes, the authors have determined the supersolubility curve, and also the freezing-point curve and the melting-point curve for the whole series of mixtures.

RESEARCH FUND.

A Meeting of the Research Fund Committee will be held in June next. Applications for Grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on, or before, Monday, 8th June, 1908.

All persons who received grants in June, 1907, or in June of any previous year, whose accounts have not been declared closed by the Council, are reminded that reports must be in the hands of the Hon. Secretaries not later than Monday, 1st June.

The Council wish to draw special attention to the fact that the income arising from the donation of the Worshipful Company of Goldsmiths is to be more or less especially devoted to the encouragement of research in inorganic and metallurgical chemistry. Furthermore, that the income due to the sum accruing from the Perkin Memorial Fund is to be applied to investigations relating to problems connected with the coal-tar and allied industries.

At the next Ordinary Meeting, **Thursday**, May **21st**, 1908, at **8.30** p.m., the following papers will be communicated:

"Hydroaromatic ketones. Preliminary note." By A. W. Crossley and C. Gilling.

"Titani-dihydroxymaleic acid and the detection of titanium." By H. J. H. Fenton.

"Some experiments on carbon at high temperatures and pressures and apparatus therefor." By R. Threlfall.

"The sulphides and oxysulphides of silicon." By I. G. Rankin and S. M. Revington.

RICHARD CLAY AND SONS, LTD., BREAD STREET HILL, E.C., AND BUNGAY, SUFFOLK.

Issued 30/5/08

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 24. No. 342

Thursday, May 21st, 1908, at 8.30 p.m., Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

Messrs. G. Barr, C. Gilling, G. R. Lynch, W. E. Oakden, D. R. Pinnock, and W. H. Withey were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs.:

William Henry Ballantyne, B.Sc., 99, Holmdene Avenue, Herne Hill, S.E.
Edward Morris Bevan, 10, Coronation Street, Aberkenfig, Glam.
James Brown, 20, Tower Road, Dartford, Kent.
James Hill Fairweather, 62, Wythes Road, Silvertown, E.
Frank William Crossley-Holland, Connaught Club, Marble Arch, W.
Alfred Ash Meggitt, B.Sc., Dacca, Eastern Bengal, India.
Clement Thomas Rutter, 4, Bath Terrace, Hanwell, W.
James Edward Southcombe, M.Sc., 138, Chester Street, Birkenhead, Cheshire.
Edward Stokes, B.A., King William's College, Isle of Man.
Harry James Yates, Redcroft, Four Oaks, Warwickshire.

A certificate has been authorised by the Council under Bye-Law I (par. 3) in favour of Hari Prasad Vidyant, Etawah, U.P., India.

Of the following papers, those marked * were read :—

*110. "Hydroaromatic ketones." (Preliminary note.)

By Arthur William Crossley and Charles Gilling.

5-Chloro-1 : 1-dimethyl-Δ^4-*cyclo*hexenone-3 (I) reacts readily with ethyl malonate in presence of sodium ethoxide to give *ethyl* 1 : 1-*dimethyl*-Δ^4-cyclo*hexen*-3-*one*-5-*acetate* (II). During the condensation,

$$CMe_2\langle\begin{matrix}CH_2-CO\\CH_2\cdot CCl\end{matrix}\rangle CH \quad (I.) \quad \longrightarrow \quad CMe_2\langle\begin{matrix}CH_2\text{————}CO\\CH_2\cdot C(CH_2\cdot CO_2Et)\end{matrix}\rangle CH \quad (II.)$$

one of the carbethoxy-groups of the ethyl malonate is evidently hydrolysed by the sodium ethoxide, and the resulting carboxyl group loses the elements of carbon dioxide (compare Moore, *Trans.*, 1904, **85**, 165).

The ester is a faintly yellow oil, boiling at 171°/22 mm. and possessing a slight ethereal odour. It gives a *semicarbazone* melting at 156—157° without decomposition. When hydrolysed with alcoholic potassium hydroxide, the corresponding acid cannot be isolated, as it at once loses carbon dioxide to give 1 : 1 : 5-*trimethyl*-Δ^4-cyclo*hexenone*-3 (III) as a colourless, highly refractive liquid, boiling at 108°/35 mm. and possessing a slight camphoraceous odour. The *semicarbazone* crystallises from alcohol in clusters of flattened needles melting at 190—191°, and the *oxime* forms large, transparent prisms melting at 78°. When oxidised with potassium permanganate, a variety of products are obtained, according to the conditions employed. One acid, melting at 98°, has been proved to have the composition $C_9H_{14}O_4$, and its constitution is most probably represented by formula IV :

$$CMe_2\langle\begin{matrix}CH_2-CO\\CH_2\cdot CMe\end{matrix}\rangle CH \quad (III.)$$

$$CMe_2\langle\begin{matrix}CH_2\text{————}CO\\CH_2\cdot C(CH_3)\end{matrix}\rangle CH \quad \longrightarrow \quad CMe_2\langle\begin{matrix}CH_2\cdot CO\cdot CO_2H\\CH_2\cdot CO\cdot CH_3\end{matrix} \quad (IV.)$$

The reaction appears to be a general one, for 5-chloro-1 : 1-dimethyl-Δ^4-*cyclo*hexenone-3 condenses with ethyl ethylmalonate in presence of sodium ethoxide, and the product on hydrolysis yields 1 : 1-*dimethyl*-5-*propyl*-Δ^4-cyclo*hexenone*-3, boiling at 125°/19 mm. and possessing an odour of celery and camphor. The *semicarbazone* crystallises from alcohol in rosettes of flattened needles melting at 156°. The work is being extended, and the products and by-products of the various reactions are under closer investigation.

$$CMe_2\langle\begin{matrix}CH_2\text{————}CO\\CH_2\cdot C(C_2H_7)\end{matrix}\rangle CH$$

***111. "The sulphides and oxysulphides of silicon." By Irvine Giles Rankin and Sidney Montagu Revington.**

The white sulphide of silicon, first prepared by Berzelius, has been shown definitely to be the disulphide, SiS_2. The orange sulphide, SiS, prepared by Colson, has been investigated, and, in addition, the composition of two sulphoxides, SiSO and $SiSO_2$, has been determined; the former is mentioned by Colson, but was not analysed by him, whilst the latter has been hitherto unknown.

Discussion.

The President congratulated Mr. Revington and Mr. Rankin on the results they had obtained. He could testify to their perseverance, and, although the analyses which they had quoted were not so concordant as is usual, the difficulties of separating and obtaining in a pure state three such bodies as SiS_2, SiOS, and SiS were great, and at present, at all events, we had to be content with what were great improvements on former results.

***112. "Apparatus for experiments at high temperatures and pressures and its application to the study of carbon." By Richard Threlfall.**

The author described a small and inexpensive laboratory apparatus for exposing carbon or other substances to very high temperatures and pressures. It was shown how small quantities of material may be heated up to the temperature of the melting point of magnesia at pressures up to 100 tons per square inch. These results are rendered possible by taking advantage of the practically perfect fluidity of crystalline graphite under high pressures. Instead of using compressed gases, as has hitherto been done in order to obtain high pressures, it is only necessary to make use of crystalline graphite, which is, of course, very much more easily and safely handled. The graphite itself acts as a conductor whereby electric heating is rendered possible.

Some experiments on heating graphite or amorphous carbon up to the melting point of magnesia at pressures up to 100 tons per square inch were described. In no case was anything produced but soft, crystalline graphite, the results obtained agreeing precisely with those already published by Parsons (*Proc. Roy. Soc.*, 1907, **79**, *A*, 532).

A summary was given of our present information in regard to the transformation of carbon, and the view is taken that the formation of diamond under certain conditions is not so much a direct transforma-

tion of carbon as the result of the liberation of carbon by decomposition of carbides in presence of certain substances which induce it to crystallise in any of the well-known forms of diamond. These substances can be recognised by a study of the ash left when diamonds are burnt. The only condition as to temperature is that it must be low enough for the velocity of transformation into graphite to be small. The results obtained by Hasslinger and others were examined from this point of view.

***113. "Acids as accelerators in the acetylation of amino-groups." By Alice Emily Smith and Kennedy Joseph Previté Orton.**

When the basic properties of amino-groups are in abeyance, acids act as powerful accelerators of acetylation by means of acetic anhydride. Such amino-groups are present in anilines with two negative groups in the ortho-positions with respect to the amino-group.

All strong acids, very small quantities of which are alone needed, act in this manner. Sulphuric, hydrochloric, perchloric, trichloroacetic, nitric, and chromic acids have been tested; the two latter behave exceptionally, yielding respectively nitroaminobenzene, $Ar{\cdot}NH{\cdot}NO_2$, and products of oxidation of the aniline.

The formation of diacetyl as well as of monoacetyl derivatives of the anilines, is aided by the presence of acids.

In the case of basic amino-groups, the reaction of which with acetic anhydride, even when largely diluted by a neutral solvent, is extremely rapid, acids act as mild inhibitors of acetylation.

Details of the preparation of typical mono- and di-acetanilides with the aid of strong acids were described.

***114. "The chemical action of radium emanation. Part III. On water and certain gases." By Alexander Thomas Cameron and Sir William Ramsay, K.C.B.**

The decomposition of water and the recombination of hydrogen and oxygen, when treated with radium emanation, have been confirmed by numerous experiments. Carbon dioxide is decomposed into carbon, oxygen, and the monoxide. The last named gives carbon, oxygen, and the dioxide. Ammonia breaks up into its components. These recombine, but in smaller quantity for the same amount of emanation. Hydrogen chloride is decomposed into hydrogen and chlorine. At 130°, hydrogen and oxygen recombine during five hours at a steady rate; steam is apparently undecomposed. The time rates of the various reactions were measured; the volume was kept constant, and

change of pressure indicated the rate of change. This was in all cases proportional to the rate of change of the emanation. In other words, it obeyed the same exponential law; the amount of change in any time was strictly proportional to the amount of emanation disintegrating in that time. Hence, other conditions being the same, each atom of emanation, as it disintegrates, produces a certain definite chemical effect.

***115. "The chemical action of radium emanation. Part IV. On water." By Alexander Thomas Cameron and Sir William Ramsay, K.C.B.**

The results obtained in a previous experiment (*Trans.*, 1907, **91**, 1593) have been confirmed; radium emanation in presence of water breaks up into neon. The neon was conclusively identified by its spectrum; the lines were almost as bright as those of the helium visible at the same time. The spectrum was photographed successfully, and a large number of the neon lines identified. It faded rapidly; the neon lines practically disappeared in ten minutes.

116. "Titani-dihydroxymaleic acid and the detection of titanium." By Henry John Horstman Fenton.

Dihydroxymaleic acid reacts in cold dilute aqueous solution with quadrivalent titanium compounds, giving an intensely reddish-brown solution. The reaction is so sensitive that it serves for the detection of minute traces of titanium. It is very much more delicate than the hydrogen dioxide test, and has the additional advantage that it is not given by vanadium.

From more concentrated solutions, a voluminous chocolate-coloured precipitate separates, which has the empirical composition

$$C_4H_4O_6,2TiO_2,2\tfrac{1}{2}H_2O.$$

This compound acts as an acid, giving, when treated with alkalis bright orange-coloured salts.

Compounds having a similar composition have previously been obtained with many other aliphatic acids, but they are all colourless.

The coloured compound obtained with dihydroxymaleic acid is at once destroyed by hydrofluoric acid or soluble fluorides, and may, as in the case of the hydrogen dioxide reaction, be employed for the detection of fluorides. Owing to the marked difference in colour between the acid and its salts, the compound may also be used as an alkali-acid indicator.

117. "The preparation of diselenides. Dibenzyl diselenide." (Preliminary note.) By Thomas Slater Price and Lionel Manfred Jones.

The method employed by Price and Twiss (*Trans.*, 1907, **91**, 2021) for the preparation of disulphides has been extended to the preparation of diselenides. A solution of sodium selenosulphate was obtained by digesting excess of selenium with a solution of sodium sulphite and then filtering. On adding this solution to an alcoholic solution of benzyl chloride, a turbid liquid was obtained, which, however, soon cleared when heated on a water-bath under reflux. After a short time, sulphur dioxide was evolved, and a small quantity of a yellow oil separated, which, after removal from the remainder of the liquid, solidified on cooling; on recrystallisation from alcohol, it was obtained in lustrous, yellow crystals, melting at 90·5°, and had all the characteristic properties of dibenzyl diselenide, as described by Jackson (*Annalen*, 1875, **179**, 1). It had probably been formed according to the following equations, the evidence for which the authors hope to publish later:

$$C_6H_5\cdot CH_2Cl + Na_2SeSO_3 = C_6H_5\cdot CH_2\cdot Se\cdot SO_3Na + NaCl.$$
$$2C_6H_5\cdot CH_2\cdot Se\cdot SO_3Na + H_2O = (C_6H_5\cdot CH_2\cdot Se)_2 + Na_2SO_4 + H_2O + SO_2.$$

On allowing the mother liquor to stand, a further quantity of diselenide slowly separated, sulphur dioxide being continuously evolved. The diselenide was also obtained from the mother liquor, after the addition of potassium hydrogen carbonate, by electrolysis in a divided cell, the method being similar to that used in the preparation of disulphides (Price and Twiss, *loc. cit.*).

118. "The optical and sensitising properties of the *iso*cyanine dyes." By Samuel Edward Sheppard.

The absorption spectre and sensitising power for gelatino-bromide plates have been investigated for a series of dyes of the *iso*cyanine group. It was shown that solutions in alcohol and chloroform conform to Beer's law, and that the colour is probably independent of ionisation. Further, in different solvents, the absorption follows Kundt's rule, the bands being shifted to the red as the dispersive power of the solvent increases. The influence of different substituted groups on the absorption and sensitising power was measured. It is found that for a group of dyes of similar chemical constitution the photochemical activity is proportional to the rate of fading in light. Comparison of the sensitising and absorption spectra shows that the bands in the

latter are regularly displaced to the red some 10 $\mu\mu$, as would be expected from their behaviour in different solvents. The investigation of the conditions of sensitising by bathing shows that the "taking-up" of the dye is an absorption process comparable with substantive dyeing.

119. **"The polarimetric study of intramolecular rearrangement in inactive substances." By Thomas Stewart Patterson and Andrew McMillan.**

Continuing previous work (*Trans.*, 1907, **91**, 504; *Ber.*, 1907, **40**, 2564), the authors have applied their new method for studying intramolecular rearrangement in inactive compounds to measure the rate of inversion of piperonal*syn*oxime at a number of temperatures. The increase of velocity with rise of temperature was found to obey van't Hoff's law. The method was also applied for the measurement of the inversion of *p*-iodobenz*syn*aldoxime in *n*-propyl tartrate and to the transformation of ω-*iso*nitrotoluene into ω-nitrotoluene, satisfactory constants being obtained. It was shown that by the same method the dynamic isomerism of ammonium thiocyanate and thiocarbamide and of ammonium cyanate and carbamide could be followed.

120. **"Mercuric zinc cyanide." A correction. By Wyndham Rowland Dunstan.**

In a paper communicated to the Society in 1892 (*Trans.*, 1892, **61**, 666), the author described the results of an investigation of the "antiseptic cyanide" which had been introduced into surgery by Lord Lister. The conclusion was arrived at that the substance was an unstable double mercuric zinc cyanide, for which the formula proposed was $Zn_4Hg(CN)_{10}$, and this was stated to correspond with 40·65 per cent. of mercuric cyanide. This is a miscalculation, as the formula actually requires 35 per cent. of mercuric cyanide, and must therefore be rejected.

The formula which most nearly corresponds with the maximum percentage of mercuric cyanide found, namely, 38·5, and which is also in accordance with the curves plotted from numerous experimental data, is $Zn(CN)_2,\frac{1}{3}Hg(CN)_2$, which requires 41·6 per cent. of mercuric cyanide.

The salt, prepared as described, may therefore be regarded as a trizincic monomercuric octacyanide of the formula $Zn_3Hg(CN)_8$, which, as shown, inevitably suffers some decomposition by the water present during its precipitation.

121. "Ethyl 6-methyl-2-pyrone-3 : 5-dicarboxylate and its derivatives." By John Lionel Simonsen.

When ethyl ethoxymethylenemalonate reacts with ethyl sodioacetoacetate, *ethyl 6-methyl-2-pyrone-3 : 5-dicarboxylate* is obtained:

$$(CO_2Et)_2{:}C{:}CH{\cdot}OEt + CHNaAc{\cdot}CO_2Et \longrightarrow (CO_2Et)_2{\cdot}C{:}CH{\cdot}CHAc{\cdot}CO_2Et.$$

$$CH\langle\begin{matrix}C(CO_2Et){\cdot}CO_2Et\\C(CO_2Et){:}CMe{\cdot}OH\end{matrix} \longrightarrow CH\langle\begin{matrix}C(CO_2Et)-CO\\C(CO_2Et){:}CMe\end{matrix}\rangle O.$$

The same product results from the interaction of (I) ethyl ethoxymethyleneacetoacetate and ethyl sodiomalonate; (II) ethyl ethoxymethyleneacetoacetate and the ethyl sodiocyanoacetate, and (III) ethyl ethoxymethylenecyanoacetate and ethyl sodioacetoacetate.

Ethyl 6-methyl-2-pyrone-3 : 5-dicarboxylate readily reacts with ammonia, with formation of *ethyl ammonium 6-hydroxy-2-methylpyridine-3 : 5-dicarboxylate*, $CH\langle\begin{matrix}C(CO_2{\cdot}NH_4){\cdot}C(OH)\\C(CO_2Et)=CMe\end{matrix}\rangle N$, which on hydrolysis with alcoholic potash yields 6-hydroxy-2-methylpyridine-3 : 5-dicarboxylic acid, $CH\langle\begin{matrix}C(CO_2H){\cdot}C(OH)\\C(CO_2H)=CMe\end{matrix}\rangle N$, which has already been described by Errera (*Ber.*, 1900, **33**, 2969). The action of aniline on ethyl 6-methyl-2-pyrone-3 : 5-dicarboxylate has also been investigated.

122. "Contributions to the chemistry of the amidines. Part II. 2-Anilinobenzoxazole and the supposed anilodihydrobenzoxazole." By George Young and Albert Edward Dunstan.

The authors have reinvestigated the two substances described in the literature as anilinobenzoxazole and anilodihydrobenzoxazole. They confirm the nature and constitution of the anilino-compound, but find that the supposed isomeride is in reality carbanilide.

The following substances were described:

Acetylanilinobenzoxazole, $C_{13}H_9ON_2Ac$, m. p. 91°, *p-chlorophenylcarbamide*, $C_7H_7ON_2Cl$, m. p. 212°, di-*p*-chlorocarbanilide, m. p. 289°, *trichlorocarbanilide*, $C_{13}H_9ON_2Cl_3$, m. p. 262°, and di-*p*-tolylcarbamide, m. p. 265°.

123. "The slow decomposition of ammonium chromate, dichromate, and trichromate by heat." By Walter Craven Ball.

When ammonium dichromate is heated at temperatures between 185° and 205°, it gradually becomes dark brown and finally black, and nitrogen, water, and ammonia are evolved. After heating for

several days, the remaining black substance has the approximate percentage composition: Cr_2O_3, 83·89; active oxygen, 9·00, and water, 6·93. This corresponds fairly well with the formula $3CrO_2,H_2O$, but the composition is not quite constant.

If the heating is interrupted at an intermediate stage, it is found that part of the dichromate has decomposed, with production of a black, insoluble substance, nearly half the nitrogen of the decomposed dichromate being contained in it. This black substance also varies in composition, but approximates to the formula $2CrO_3,Cr_2O_3,2NH_3,H_2O$.

The slow decomposition of ammonium dichromate is therefore partly a dehydration to this insoluble compound containing ammonia, and partly a combustion of the hydrogen of the ammonium to form water, with production of nitrogen.

The author has studied quantitatively the decomposition of ammonium chromate and of ammonium trichromate under similar conditions; the substances decompose in a similar manner.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Bloxam, *W. Popplewell.* Report to the Government of India, containing an account of the research work on indigo performed in the University of Leeds, 1905—1907, by *W. Popplewell* **Bloxam**, with the assistance of *S. H.* **Wood**, *I. Q.* **Orchardson**, *R.* **Gaunt**, and *F.* **Thomas**; and under the general supervision of *A. G.* **Perkin**. pp. 117. 1908. (*Recd.* 19/5/08.) From His Majesty's Secretary of State for India.

Institute of Chemistry of Great Britain and Ireland. A list of official chemical appointments compiled, . . . by *Richard B.* **Pilcher**. Second edition. pp. 172. London 1908. (*Reference.*)
From the Institute of Chemistry.

Landauer, *John.* Spectrum analysis. Authorised English translation by *J. Bishop* **Tingle**. Second edition. pp. ix + 236. New York 1907. (*Recd.* 13/5/08.)
From the Publishers: Messrs. John Wiley & Sons.

National Physical Laboratory. Collected researches. Vols. II. and III. pp. 286, 252. ill. [London] 1908. (*Recd.* 16/5/08.)

——— Report for the year 1907. pp. 97. ill. Teddington 1908.
From the National Physical Laboratory.

Richardson, *S. S.* Magnetism and electricity, and the principles of electrical measurement. pp. viii + 596. ill. London 1908. (*Recd.* 14/5/08.) From the Publishers: Messrs. Blackie & Son.

United States. *Public Health and Marine-Hospital Service. Hygienic Laboratory.* Bulletin No. 41. Milk in its relation to the public health. By various authors. pp. 756. ill. Washington 1908. (*Recd.* 4/5/08.) From the Surgeon-General.

II. *By Purchase.*

Brouchuisius, *Daniel.* Secreta Alchimiæ Magnalia D. Thomæ Aquinatis, De Corporibus supercœlestibus, & quòd in rebus inferioribus inveniantur, quoque modo extrahantur: De Lapide minerali, animali, & plantali. Item Thesaurus Alchimiæ secretissimus; quem dedit frati suo Reinaldo. Accessit et Ioannis De Rupescissa Liber lucis, ac Raymundi Lullij opus pulcherrimum, quod inscribitur Clavicula & Apertorum in quo omnia quæ in opere Alchimiæ requiruntur, venustè declarantur, & sine quo, ut ipse testatur Lullius, alij sui Libri intelligi neqeunt. Opuscula studiosis artis secretissimæ, ut summè necessaria, ita lectu iucundissima . . . Cum Præfatione D. Ioannis Heurnij. Lugduni Batavorum, Ex Officinâ Thomæ Basson 1598. pp. 71. 1 plate. (*Reference.*)

Carrara, *G.* Elektrochemie der nichtwässrigen Lösungen. Uebersetzt von *Kurt* **Arndt**. (Sammlung, Vol. XII.) Stuttgart 1908. (*Recd.* 27/4/08.)

Congrès international de chimie appliquée. Bruxelles-Anvers, 4-11 Août 1894. Compte rendu. pp. ccxxxi + 302. Bruxelles 1894. (*Recd.* 14/5/08.)

——— Paris. Compte rendu in-extenso. 3 vols. pp. 622, 788, 472. Paris 1902. (*Recd.* 14/5/08.)

Hjelt, *Edv.* Berzelius-Liebig-Dumas. Ihre Stellung zur Radikaltheorie 1832—1840. (Sammlung, Vol. XII.) Stuttgart 1908. (*Recd.* 27/4/08.)

Hofmann, *A. W.* Biographie de Jean Baptiste André Dumas, avec complément. pp. 74, 14. Paris 1880, 1885. (*Recd.* 14/5/08.)

Mynsicht, *Hadrianus à.* Thesaurus et Armamentarium Medico-Chymicum. In quo selectissimorum contra quosuis morbos Pharmacorum conficiendorum secretissima ratio aperitur, unà cum eorumdem Virtute, Usu, & Dosi. Cui in fine adjunctum est Testamentum Hadrianeum de Aureo Philosophorum lapide. Editio tertia emendatior. Venetiis, 1696. pp. [xvi] + 490 + [xlii]. (*Reference.*)

Ruer, *Rudolf.* Metallographie in elementarer Darstellung. pp. xii + 312. ill. Hamburg 1907. (*Recd.* 20/5/08.)

Ubbelohde, *L.* Handbuch der Chemie und Technologie der Oele und Fette. Chemie, Analyse, Gewinnung und Verarbeitung der Oele, Fette, Wachse und Harze. Band I. pp. xiv + 832. ill. Leipzig 1908. (*Recd.* 20/5/08.)

Vorländer, *D.* Kristallinisch-flüssige Substanzen. (Sammlung, Vol. XII.) Stuttgart 1908. (*Recd.* 30/3/08.)

Watts, *W. Marshall.* Index of spectra. Appendix S. pp. 155. London 1908. (*Recd.* 14/5/08.)

Zeitschrift für wissenschaftliche Photographie Photophysik und Photochemie. Vol. VI, &c. Edited by *K.* **Schaum.** Leipzig 1908 + . (*Reference.*)

RESEARCH FUND.

A Meeting of the Research Fund Committee will be held in June next. Applications for Grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on, or before, Monday, 8th June, 1908.

All persons who received grants in June, 1907, or in June of any previous year, whose accounts have not been declared closed by the Council, are reminded that reports must be in the hands of the Hon. Secretaries not later than Monday, 1st June.

The Council wish to draw special attention to the fact that the income arising from the donation of the Worshipful Company of Goldsmiths is to be more or less especially devoted to the encouragement of research in inorganic and metallurgical chemistry. Furthermore, that the income due to the sum accruing from the Perkin Memorial Fund is to be applied to investigations relating to problems connected with the coal-tar and allied industries.

At the next Ordinary Meeting, Thursday, June 4th, 1908, at 8.30 p.m., the following papers will be communicated:

"Condensation products from pinene aminodicarboxylic acid." By W. Godden.

"A delicate test for bromides alone, or in solution with chlorides." By J. S. Jamieson.

"Experiments on the synthesis of 1-methyl*cyc*lohexylidene-4-acetic acid." By W. H. Perkin and W. J. Pope.

"The triazo-group. Part IV. Allylazoimide." By M. O. Forster and H. E. Fierz.

RICHARD LAY AND SONS, LTD., BREAD STREET HILL, E.C. AND BUNGAY, SUFFOLK.

Issued 16/6/08

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 24. **No. 343**

Thursday, June 4th, 1908, at 8.30 p.m., Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

Mr. J. Gibson was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. :

Thomas Aubertin, B.A., c/o Messrs. George Anderson & Co., Ltd., Carnoustie, N.B.
John William Pearson, B.A., Buxton College, Buxton.
Frank Perry, 63, Tunnel Street, Coseley, near Bilston, Staffs.
George O'Brien Power, Fatehpur, U.P. of Agra & Oudh, India.
William Frothingham Roach, M.D., M.S., Royal Mersey Yacht Club, Rock Ferry, Cheshire.

Of the following papers, those marked * were read :—

*124. **"The interaction of copper and nitric acid in presence of metallic nitrates considered with reference to the existence of hydrates in solution." By Edward Henry Rennie, Alfred James Higgin, and William Tennant Cooke.**

The authors find that in most cases the addition of metallic nitrates greatly accelerates the dissolution of copper in nitric acid, but that nitrates, such as those of rubidium and cæsium, cause considerable retardation. They consider that these effects are due to the withdrawal by the salts of water or nitric acid from the solution, and the

consequent concentration or dilution of the acid, and regard their results as confirmatory of the views now generally held that combination takes place between solvent and solute. They find, moreover, that the accelerations produced by the nitrates of any one group of metals decrease as the atomic weights of the metals increase. When copper nitrate is added to the nitric acid, the dissolution is greatly accelerated. Hence the view that the auto-acceleration always observed when copper is dissolved in nitric acid is due to nitrous acid requires to be modified, the accumulation of copper nitrate in the solution being an important factor in the progress of the change.

Discussion.

Dr. Veley remarked that the results obtained by the authors might in some cases be due, not to the nitrates *per se*, but also to the nitrous acid or nitrites formed therefrom. Thus, when the conditions are such that copper dissolves in nitric acid (containing nitrous acid), copper nitrite is initially formed, which is subsequently converted into the nitrate. It appeared to him that it would be of interest if the authors were to extend their investigations to metals other than copper, such as mercury, which dissolves initially as mercurous nitrite, yielding mercurous nitrate and, finally, mercuric nitrate under certain conditions. Silver and bismuth behave generally as copper.

Mr. W. C. Reynolds pointed out that nitric acid, with or without the presence of nitrates, has no action whatever on metallic copper if it is freed from traces of nitrous acid, even in the case of much stronger acid than that referred to. This could be effected in a few seconds at the ordinary temperature by adding a trace of sodium peroxide to the acid solution—the addition of carbamide was not so effective.

The alkaloids, morphine, and especially brucine, afford colour tests for the presence of nitrous acid in such acid solutions, and the addition of either should cause no coloration for some hours in the absence of nitrous acid (Reynolds and Sutcliffe, *J. Soc. Chem. Ind.*, 1906, **25**, 512). He thought some of the apparently anomalous results obtained by the authors might be due to the varying amount of the "trace" present.

Prof. Armstrong (who had given an account of the paper) said that, whilst he was in accord with the authors that salts exercised a "concentrating effect," he did not think that the acceleration observed was due to the direct withdrawal of water from the nitric acid; the acid used was too dilute and the proportion of salt too small to account, on such an assumption, for the effects produced. It was, however, well known that the dissolution of copper was dependent on

the presence of nitrous compounds, and he was inclined to think that salts produced their effect by modifying the condition of these compounds in solution. From this point of view, the observations were most striking and valuable as throwing fresh light on the changes involved in the dissolution of metals in presence of nitric acid.

As to the influence of copper nitrate, it was to be remembered that the heat of dissolution of copper in nitric acid is a negative quantity, and that, from this point of view, copper nitrate is a more effective solvent of copper than the acid.

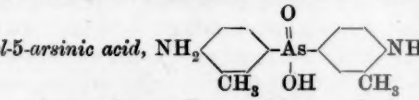
*125. "The triazo-group. Part IV. Allylazoimide."
By Martin Onslow Forster and Hans Eduard Fierz.

Allylazoimide, $CH_2{:}CH{\cdot}CH_2{\cdot}N_3$, prepared with some difficulty from allyl chloride and sodium azide, is a mobile, refractive liquid which boils at 76·5° under 760 mm. pressure; owing to subsidiary changes, the yield is disappointing. The *dibromide*, $C_3H_5N_3Br_2$, is a heavy, colourless liquid, boiling at 87° under 5 mm. pressure.

The diazoamino-*compound*, $C_3H_5N_3$, arises from allylazoimide by spontaneous isomeric change, crystallising from the liquid azoimide in colourless, transparent, lustrous prisms which melt and decompose at 192°; the substance is bimolecular, and is remarkably sensitive towards dilute acids, including acetic, which liberate two-thirds of the nitrogen in elemental form.

*126. "Aromatic arsenic and arsinic acids."
By Frank Lee Pyman and William Colebrook Reynolds.

In the preparation of *p*-aminophenylarsonic acid and 2-aminotolyl-5-arsonic acid, the corresponding bisaminoarylarsinic acids, which have been briefly alluded to by Benda and Kahn (*Ber.*, 1908 41, 1672), were obtained. The isolation of these by-products was described, and the following new substances were characterised.

Bis-2-aminotolyl-5-arsinic acid,  , forms highly refracting, microscopic needles, melting and decomposing at 247—249°. The *sodium* salt forms large, hard, prismatic needles, which melt at 74—75° and contain $7\frac{1}{2}$ molecular proportions of water of crystallisation.

Bis-2-acetylaminotolyl-5-arsinic acid, $C_{18}H_{21}O_4N_2As,\frac{2}{3}H_2O$, crystallises from water in highly refracting, microscopic prisms, melting at 242—244°.

Its *sodium* salt forms radial clusters of silky needles, which melt at 106—107° and contain 6 molecules of water of crystallisation.

Bis-p-*aminophenylarsinic acid*, $C_{12}H_{13}O_2N_2As$, forms matted needles, melting at 248—249°. Its *sodium* salt crystallises in large, monoclinic plates, containing between 5 and 6 molecular proportions of water of crystallisation; its *barium* salt forms large, hard prisms containing $7\frac{1}{2}$ molecular proportions of water of crystallisation.

Bis-p-*acetylaminophenylarsinic acid*, $C_{16}H_{17}O_4N_2As,3H_2O$, crystallises from water in rosettes of needles, and melts at 275°. Its *sodium* salt forms prismatic needles containing 9 molecules of water of crystallisation.

Discussion.

The President inquired whether, in view of the fact that antimony compounds appeared to be more effective than arsenic compounds as a remedy for sleeping sickness, any attempts had been successful to form similar compounds with antimonic acid?

Dr. Pyman replied that no such attempts had as yet proved successful.

127. "Condensation products from aminopinenedicarboxylic acid." By William Godden.

Condensation products of glycine and aspartic acid with aminopinenedicarboxylic acid have been obtained, and their copper salts prepared.

128. "A delicate test for bromides alone or in solution with chlorides." By James Sprunt Jamieson.

The solution to be tested is heated to boiling with 1 or 2 c.c. of dilute sulphuric acid and 1 or 2 c.c. of potassium dichromate; it is then cooled, and shaken with chloroform. The chloroform layer is separated, washed two or three times with water, and finally shaken with a little dilute potassium iodide solution. In the presence of a bromide, the chloroform is coloured violet, due to the liberated iodine.

The following equation probably represents the reaction:

$$6NaBr + K_2Cr_2O_7 + 7H_2SO_4 = 3Na_2SO_4 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3Br_2.$$

The above reaction will detect 0·5 milligram of sodium or potassium bromide, either free or in presence of sodium chloride.

129. "**Experiments on the synthesis of 1-methyl*cyclo*hexylidene-4-acetic acid, $CHMe<^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}>C{:}CH\cdot CO_2H$. Part I.**" **By William Henry Perkin, jun., and William Jackson Pope.**

The authors have continued the work of which a preliminary account has already appeared (*Proc.*, 1906, **22**, 107).

130. "**A method for the measurement of rate of change in solid alloys.**" **(Preliminary note.) By Guy Dunstan Bengough.**

The method consists in heating portions of the metastable alloy at a selected temperature for various lengths of time. The portions are then quenched in water to stereotype as far as possible the phases present at the selected temperature. Photomicrographs are made at a magnification determined by the coarseness of the crystalline structure. From the entire negative, an enlargement is made on bromide paper, the degree of enlargement again depending on the coarseness of the structure. The relative proportions of the phases present may then be determined by cutting them out separately and weighing. Curves are then plotted with axes representing time and percentages of any given constituent, showing the rate of change at the selected temperature.

Tests made on the uniformity of the bromide paper used for the enlargement and on the difference in weight between portions of the paper which printed black and white respectively have shown that the errors due to these causes are negligibly small when compared with some others inherent in the process.

Duplicate measurements of the percentage of one of the constituents in a copper-zinc alloy gave the following results:

Alloy.	Proportion of α-constituent.	Mean.
Cu, 60 per cent. Zn, 40 ,,	i. 67·3 ii. 67·7	67·5
Another specimen of same alloy	i. 67·5 ii. 67·7	67·6
Another specimen annealed 7 hours at 540° and slowly cooled	i. 89·2 ii. 89·3	89·25

By careful selection of typical portions of the alloy, and with crystalline structures suitable to the method, the limit of accuracy appears to be about ± 0·25 per cent.

Comparative tests have been made to ascertain how far planimetric

measurements of the areas of the phases after enlargement agree with the results obtained by the method described:

Alloy.	Proportion of α-constituent.		Mean.
Cu, 60 per cent. Zn, 40 ,,	By planimeter	59·2 ; 58·5	58·85
	By weighing	59·6 ; 60·0	59·8
Same, annealed at 640° and slowly cooled	By planimeter	64·6 ; 64·2	64·4
	By weighing	65·3 ; 64·6	64·95

The planimeter gives the lower result in both cases, for a reason not yet ascertained. The actual proportions of the α constituent in the above experiments have no significance; they depend on the rate of cooling adopted in the various experiments. The particular alloys used have merely been chosen to test the method of measurement proposed.

Huntington and Desch have very recently (April 28, 1908) read a paper before the Faraday Society on the "Planimetric Analysis of Alloys," and their work has come to the author's notice since his own results were obtained. They consider the planimetric measurement of the areas to be more accurate and preferable to weighing. The present author considers the weighing method to be preferable for many kinds of structure, and to be susceptible of considerable accuracy. The author is using it for the measurement of rate of change in copper-zinc alloys.

131. "Viscosity determinations at high temperatures." By Charles Edward Fawsitt.

The viscosity of some fused salts and metals has been measured by the method recently described by the author (*Proc. Roy. Soc.*, 1908, **80**, *A*, 290). The absolute viscosities of sodium nitrate, potassium nitrate, sodium chloride, potassium chloride, sodium bromide, potassium bromide, and lithium chloride have been determined over a considerable range of temperature. The best comparison of the viscosities of salts is obtained by choosing in all cases the values at the melting points, or at temperatures equally distant from the melting points. The viscosity of a sodium salt at its melting point is very nearly the same as the viscosity of the corresponding potassium salt. The viscosity of the salts examined was in no case greater than 0·03 (C.G.S. units); as the viscosity of water at 20° is 0·01, the viscosity of these salts is really not so much greater, as might have been expected. The viscosity of a mixture of sodium and potassium nitrates shows a maximum value at the composition corresponding with the eutectic mixture, provided the comparison is made at temperatures equally distant from the melting points. The viscosity of a salt decreases with rise of temperature. The

temperature-coefficients of these salts are proportional to their viscosities. Metals have also a small viscosity. Lead and tin at their melting points are only about three times as viscous as water. Bismuth and mercury have only about twice the viscosity of water. When a molten metal is cooled to its solidifying point, there is no abrupt or large increase in the viscosity to indicate the approach of the solid state. The change from the liquid to the solid state corresponds with a sudden and violent change in viscosity.

132. "Dinitrodiphenylamine-*o*-sulphonic acids." (Preliminary note.) By Samuel Smiles.

By heating 2-chloro-5-nitrobenzenesulphonic acid with the nitroanilines, the corresponding diphenylamine-*o*-sulphonic *acids* are formed. The acids may be isolated as the sparingly soluble, yellow *sodium* salts in a yield equal to about 20—25 per cent. of the theoretical. These substances have been prepared with a view to effecting the synthesis of the diphenylamine sulphoxides.

133. "The study of the absorption spectra of the hydrocarbons isolated from the products of the action of aluminium chloride on naphthalene." By Annie Homer and John Edward Purvis.

In an investigation of the action of aluminium chloride on naphthalene, one of the authors isolated, besides Friedel & Crafts' $\beta\beta$-dinaphthyl, three new hydrocarbons, $C_{14}H_{16}$, $C_{26}H_{22}$, and $C_{40}H_{26}$ (*Trans.*, 1907, **91**, 1103). In the hope of obtaining additional evidence as to the constitution of these substances, a comparative study of their absorption spectra with that of naphthalene has been made. The absorption spectrum of the hydrocarbon $C_{26}H_{22}$, which was supposed to be an alkyl derivative of dinaphthanthracene, $C_{22}H_{14}$, has also been compared with those of dinaphthanthracene and picene.

The absorption curves for these hydrocarbons show that:

1. The hydrocarbon $C_{14}H_{16}$ is a naphthalene derivative.
2. The hydrocarbon $C_{40}H_{26}$ has a constitution similar to that of $\beta\beta$-dinaphthyl.
3. The isomeric hydrocarbons, picene, and dinaphthanthracene have markedly different absorption curves.
4. The hydrocarbon $C_{26}H_{22}$ is an alkyl derivative of picene and not of dinaphthanthracene, as had been previously suggested.

134. "The synthesis and constitution of certain pyranol salts related to brazilein and hæmatein." By William Henry Perkin, jun., Robert Robinson, and [in part] Maurice Russell Turner.

The authors have continued the work of which a preliminary account has already appeared (*Proc.*, 1907, **23**, 149).

135. "Brazilin, hæmatoxylin, and their derivatives. Part IX. On Brazilein, hæmatein, and their derivatives." By Paul Engels, William Henry Perkin, jun., and Robert Robinson.

The authors have continued the investigation of which a preliminary account has already appeared (*Proc.*, 1907, **23**, 166, 291).

136. "The effect of constitution on the optical activity of nitrogen compounds." By Reginald W. Everatt.

Three substituted ammonium iodides containing the *n*-butyl group, namely, phenylmethyl-*n*-butylallyl, *p*-bromophenylbenzylmethyl-*n*-butyl, and *p*-bromophenylmethyl-*n*-butylallylammonium iodides, and also *p*-bromophenylbenzylmethylallylammonium iodide have been resolved. The first three were required to fill up gaps in the series already examined (Thomas and Jones, *Trans.*, 1906, **89**, 280; Jones and Hill, *Trans.*, 1908, **93**, 295), whilst the fourth was needed for purposes of comparison with the phenylbenzylmethylallylammonium iodide of Pope and Peachey (*Trans.*, 1899, **75**, 1127). The camphorsulphonic acids failed to effect resolution in the case of the third compound mentioned, which was successfully accomplished by means of both camphoric and tartaric acids.

The values obtained for the ammonium salts containing the radicles named are as follows:

	$[M]_D$ for basic ion.	$[M]_D$ for iodide in alcohol.	$[M]_D$ for iodide in chloroform.
Phenylmethyl-*n*-butylallyl	85·6°	105·1°	123·0°
p-Bromophenylmethyl-*n*-butylallyl..	98·0	114·3	187·9
p-Bromophenylbenzylmethyl-*n*-butyl	−308·7	−354·2	−481·5
p-Bromophenylbenzylmethylallyl ...	−191·1	−242·1	−346·0

In all the cases previously examined, the value of $[M]_D$ for the iodide in chloroform is greater than in alcohol; $[M]_D$ for the iodide in alcohol is greater than $[M]_D$ for the ion in water, and the chloroform solution becomes inactive, owing to racemisation.

These relations hold in the above cases, which were, however, peculiar in that the rapidity of racemisation in chloroform was much greater than usual, none of the above compounds requiring more than twenty-four hours, and some considerably less, for complete racemisation.

137. "The electrolytic oxidation of some hydroxybenzoic acids." By Arthur George Perkin and Frederick Mollwo Perkin.

Sodium purpurogallincarboxylate, $C_{11}H_7O_5\cdot CO_2Na,4H_2O$, obtained by the electrolytic oxidation of gallic acid, forms orange-brown leaflets, and this with potassium acetate gives the *potassium* salt, $C_{11}H_7O_5\cdot CO_2K,3H_2O$, crystallising in prismatic needles. The *barium* salt, $(C_{12}H_7O_7)_2Ba$, crystallises similarly.

Methyl tetramethylpurpurogallincarboxylate, $C_{12}H_3O_7(CH_3)_5$, forms pale yellow needles, m. p. 120—121°, and on hydrolysis furnishes the *acid*, $C_{12}H_4O_7(CH_3)_4$, yellow needles, m. p. 182—183°. Purpurogallincarboxylic acid by boiling with concentrated potassium hydroxide solution is converted into *purpurogallonecarboxylic acid*, $C_{11}H_7O_5\cdot CO_2H$, yellow needles melting above 360°, which separate both in the anhydrous form and with two molecules of water. On acetylation, *acetylanhydropurpurogallonecarboxylic acid*, $C_{12}H_4O_6\cdot(C_2H_3O)_2$, is produced in colourless needles, m. p. 236—238°, which on hydrolysis is reconverted into purpurogallonecarboxylic acid.

Methyl tetramethylpurpurogallonecarboxylate,

$$C_{11}H_3O(O\cdot CH_3)_4\cdot CO_2\cdot CH_3,$$

colourless prisms, m. p. 110—111°, and the corresponding *acid*, $C_{12}H_4O_7(CH_3)_4$, prisms, m. p. 166—167°, were described. By the electrolytic oxidation of gallic acid in 60 per cent. sulphuric acid (compare D.R.-P. 85390), flavellagic acid, $C_{14}H_6O_9$ (*Trans.*, 1906, **89**, 251), is obtained, whereas protocatechuic acid gives catellagic acid, $C_{14}H_6O_8$ (*loc. cit.*), but the yields do not compare favourably with those previously obtained by means of persulphates. The best results with gallic acid were obtained by employing a platinum tube as anode and, passing cold water through it, using a divided cell. A current density of 0·22 ampere per square centimetre at 7—8 volts was employed, and the yield of flavellagic acid varied from 35 to 40 per cent.

For the preparation of sodium purpurogallincarboxylate, the electrolyte employed was 15 per cent. sodium acetate, and the best results were obtained without the employment of a divided cell. The solution was vigorously agitated during the electrolysis, the current density being 0·75 ampere per square dcm. and the *E.M.F.* 5—6 volts.

138. "Note on morindin." By Arthur George Perkin.

Morindin (*Morinda citrifolia*) according to Oesterle and Tisza (*Arch. Pharm.*, 1907, **245**, 534) possesses the formula $C_{27}H_{30}O_{15}$, not $C_{26}H_{28}O_{14}$ as suggested by Thorpe and Greenall (*Trans.*, 1887, **51**, 52),

and gives an acetate, $C_{27}H_{21}O_{15}(C_2H_3O)_9$, m. p. 236—237°, readily soluble in alcohol. An examination of morindin (*Morinda umbellata*) by the author gave results agreeing with the older formula, $C_{26}H_{28}O_{14}$ (Found, C = 55·37; H = 5·14). The acetyl derivative, prepared by adding pyridine to the substance in acetic anhydride and boiling for three hours, forms pale yellow needles, m. p. 246—248°, very sparingly soluble in alcohol, and possessing the formula

$$C_{26}H_{20}O_{14}(C_2H_3O)_8$$

(Found, C = 56·01; H = 5·14, and, on hydrolysis, acetic acid = 53·60, morindone = 29·84, 29·99). The morindone thus produced was pure (Found, C = 66·64; H = 3·90). Morindin acetate was unaltered by long digestion with acetic anhydride, and was also formed when the method given by Oesterle and Tisza (*loc. cit.*) was employed. The sugar obtained by hydrolysis of the glucoside gave an osazone, m. p. 202—203°, sparingly soluble in alcohol, whereas that described by Oesterle and Tisza is readily soluble, and melts at 197°. Independent analyses of morindin carried out for the author at the University, Manchester, gave C = 55·10, 55·10; H = 5·00, 5·20 per cent., and it thus seems likely that the morindin present in the *Morinda citrifolia* is not identical with that contained in the *Morinda umbellata*.

139. "Some esters of arsenious acid." By William Robert Lang, John Francis Mackey, and Ross Aitken Gortner.

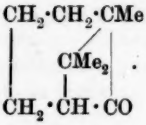
The authors have heated a number of alcohols and phenols in contact with arsenious oxide, using a reflux condenser with a Soxhlet attachment containing anhydrous copper sulphate to remove the water formed in the reaction $6ROH + As_2O_3 = 2R_3AsO_3 + 3H_2O$, otherwise a condition of equilibrium is set up at a point where only a small portion of ester has been formed. Anhydrous copper sulphate has also been employed mixed with the alcohol and arsenious oxide in the cold with good results. The following esters have been prepared in large quantities; they all decompose with water, and are capable of dissolving considerable amounts of the arsenious oxide:

	Percentage yield with anhydrous copper sulphate.	
	In Soxhlet.	Mixed together cold.
Propyl arsenite	56·75	14·8
*iso*Butyl arsenite	56·25	15·8
Trimethylcarbinol arsenite	54·27	—
Amyl arsenite	54·00	—
*iso*Amyl arsenite	58·62	17·2
Phenyl arsenite	60·00	—

Yields of 33·8 per cent. and 4·5 per cent. of methyl and ethyl arsenites respectively were obtained also, and it is found that ethyl alcohol has a much greater attraction for water than methyl or the higher alcohols, which accounts for the smallness of the yield in its case. In addition to those mentioned above, esters with the three cresols, naphthol, benzyl alcohol, the dihydric and trihydric phenols, and with methyl salicylate have all been prepared, but not quantitatively; the reaction takes place very readily. A method of analysis for the phenyl ester by titration with iodine and with dichromate was worked out and gives accurate results.

140. "α-Methylcamphor and fenchone." By Walter Hamis Glover.

The general chemical behaviour of α-methylcamphor has been contrasted with that of fenchone, and it is shown that the two substances are essentially different; thus, α-methylcamphor, unlike fenchone, is readily brominated, yielding α′-bromo-α-methylcamphor (Minguin, *Compt. rend.*, 1903, **136**, 751), and is also easily converted into a β-sulphonic acid. Fenchone, therefore, cannot possess the constitution assigned to it by Wallach (*Annalen*, 1898, **300**, 319); objections may also be raised to Semmler's formula (*Chem. Zeit.*, 1905, **29**, 1313). It is suggested that the following formula better represents the behaviour of fenchone:



The following new derivatives of α-methylcamphor have been prepared; they are very similar to the corresponding derivatives of *d*-camphor.

α′-Bromomethyl-α-methylcamphor, $C_{10}H_{14}Br(CH_2Br)O$, crystallises in colourless, silky needles, m. p. 108—109°, $[\alpha]_D^{20}$ +117·5° in benzene. *α-Methylcamphor-β-sulphonic acid*, $C_{10}H_{14}MeO{\cdot}SO_3H$, forms large, deliquescent, colourless prisms, m. p. 114—116° (decomp.), $[\alpha]_D^{20}$ +18·7° in water; the *barium* salt, $(C_{11}H_{17}O_4S)_2Ba,6H_2O$, forms large, thick, transparent, hexagonal plates, m. p. 66°; the *sulphonyl chloride*, $C_{11}H_{17}O{\cdot}SO_2Cl$, crystallises in transparent, prismatic needles, m. p. 33°, $[\alpha]_D^{20}$ +29·5° in benzene; the *sulphonamide*, $C_{11}H_{17}O{\cdot}SO_2{\cdot}NH_2$, crystallises in long, silky needles, m. p. 150°, $[\alpha]_D^{20}$ −6·3° in chloroform; the *sulphonanhydramide*, $C_{11}H_{15}ONS$, is a fine, crystalline powder, m. p. 167·5°. *β-Bromo-α-methylcamphor*, $C_{11}H_{17}OBr$, crystallises in white, silky needles, m. p. 55°, $[\alpha]_D^{25}$ +18·8° in ethyl alcohol. *α-Methyl-*

camphoroxime, $C_{11}H_{18}$:NOH, crystallises in long, slender needles, m. p. 55°, $[\alpha]_D^{20}$ +30·3°; the *hydrochloride*, $C_{11}H_{19}ON,HCl$, forms silky needles, m. p. 138° (decomp.). *Methylcampholenonitrile* is an oil with a peppermint-like odour, b. p. 226—228°.

141. "Ester hydrolysis and theories of esterification." By Arthur Lapworth.

The author has recently pointed out (*Proc.*, 1908, **24**, 101) that, whilst the initial velocity of hydrolysis of ethyl formate in acetone with hydrogen chloride as catalyst is roughly proportional to the respective concentrations of mineral acid and ester, it is hardly dependent on the amount of water present within a range of 4—20 per cent., and concluded that this afforded definite proof of the incorrectness of the theory advanced by Stieglitz, which demands a proportionality between the velocity and the concentration of the water. This conclusion was erroneous, because the possibility remains that the water so affects the medium (compare following note) that the effects due to its possible depressing effect on the reaction velocity, to the altered ionisation of the mineral acid, and to its own increased concentration exactly neutralise one another. It must be noted that the striking coincidence must be assumed to apply in alcoholic solution within similar limits as the results of Kistiatowski show (*Zeitsch. physikal. Chem.*, 1898, **27**, 253, *et seq.*).

Reference must here be made to the experiments of Ostwald (*J. pr. Chem.*, 1883, [ii], **28**, 463), in which the effect of replacing some of the water by acetone during ester catalysis was found to be very small.

The observed increase on the velocity of catalysed esterification with increase of alcohol concentration in acetone and water (see following note), as well as in water (van't Hoff; Kistiatowski), makes it appear very probable that the suggestion of Acree and Johnson (*Amer. Chem. J.*, 1907, **38**, 344), namely, that the alcohol and water enter into these reactions as neutral components in a complex ion formation, is correct; as an alternative it is possible (Stieglitz, *ibid.*, 1908, **39**, 60; Acree and Johnson, *loc. cit.*) that both ions of these compounds act simultaneously, but this seems less acceptable. It is not necessary, however, a priori, either for chemical or mathematical reasons, to suppose that during reactions in which carbonyl compounds take part under the influence of mineral acids it is the instantaneously formed oxonium ions which are directly concerned, and the fallacy in this assumption is obvious when it is remembered that the measured velocity of bromination of acetone (*Trans.*, 1904, **85**, 31, *et seq.*) is that of a

change induced in the carbonyl compound itself by the mineral acid before the bromine enters into the reaction at all; something similar is not excluded in esterification.

142. "Experiments on the formation and hydrolysis of esters, acetals, and allied compounds." (Preliminary note.) By Edward Fitzgerald and Arthur Lapworth.

At 18·2°, the initial velocity of hydrolysis of methyl acetate is nearly independent of the concentration of the water within the limits 4—30 per cent. in acetone.

During esterification by ethyl alcohol in acetone or ether, the velocity for a short time is roughly proportional to the concentration of the alcohol. In acetone, which appears to take no part in the reaction, alcohol depresses the initial velocity of hydrolysis of methyl acetate, but the effect of water on the reverse reaction is much greater, and the speed of esterification of acetic acid is, very roughly, inversely proportional to the concentration of water within the limits 4—20 per cent. This appears to lend considerable support to the supposition that the velocity of hydrolysis of an ester is intrinsically proportional to the concentration of the water, but is proportionately depressed by its action on the medium and the ionisation of the hydrogen chloride, but this leaves no room for the depression which water might produce on the velocity of esterification by sharing the intermediate products with the alcohol. (Depression of the velocity of esterification by water was noticed by Goldschmidt, Kistiatowski, and others.)

Methods of estimating the speed of hydrolysis of acetals and of ethyl orthoformate have been devised. The latter is hydrolysed by $N/1000$ hydrochloric acid at a speed which is too great to be followed, but in $N/5000$ hydrochloric acid (or in $N/10$ acetic acid to which an equivalent of sodium acetate has been added) the change into alcohol and ethyl formate can be traced; the velocity is more than 10,000 times as great as that of the hydrolysis of ethyl formate.

In all the above experiments, hydrogen chloride was used as catalyst, and the temperature was constant within 0·05°.

The equilibrium "constant" for esterification in acetone shows irregularities similar to those seen when acetone is absent, the proportion of ester being altered to an unexpectedly small extent by addition of excess of alcohol.

It is hoped that the ionisation factor of hydrogen chloride in the media employed having been ascertained, a further study of the reactions will throw some light on these questions.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Clausen, *Carl Conrad.* Ueber Eigenschaften des Chloral-Hydrates und -Alkoholates in Erweiterung der Mauch'schen Studie (1898), und unter Beiziehung der entsprechenden Bromverbindungen. pp. 191. Mülhausen 1907. (*Recd.* 14/5/08.) From Professor Dr. E. Schär.

Holleman, *A. F.* A text-book of organic chemistry. Translated from the third Dutch edition by *A. Jamieson* **Walker,** assisted by *Owen E.* **Mott.** Second English edition, rewritten. pp. xviii + 589. ill. New York 1907. (*Recd.* 30/5/08.).

From the Publishers: Messrs. John Wiley & Sons.

II. *By Purchase.*

Goerens, *Paul.* Introduction to metallography. Translated by *Fred* **Ibbotson.** pp. x + 214. ill. London 1908. (*Recd.* 25/5/08.)

Haber, *F.* Thermodynamics of technical gas-reactions. Seven lectures. Translated by *Arthur B.* **Lamb.** pp. xix + 356. ill. London 1908. (*Recd.* 25/5/08.)

Holley, *Clifford Dyer,* and **Ladd,** *E. F.* Analysis of mixed paints, color pigments, and varnishes. pp. xi + 235. ill. New York 1908. (*Recd.* 25/5/08.)

Schmidt, *Julius.* Synthetisch-organische Chemie der Neuzeit. pp. x + 185. Braunschweig 1908. (*Recd.* 25/5/08.)

III. *Pamphlets.*

Beveridge, *W. W. O.,* and **Fawcus,** *H. B.* Experiments with preserved meat. (From the *J. Roy. Army Medical Corps,* 1908.)

Carnegie Institution of Washington. *Geophysical Laboratory.* Annual report of the Director, 1907. (From the *Yearbook of the Carnegie Institution,* 6, 1908.)

Fairley, *Thomas.* The early history of distillation. (From the *J. Inst. Brewing,* 13, 1907.)

Hendrick, *James.* Improvement of hill pasture as determined by the effect on stock. Experiments in Scotland. Second report. (From the *Trans. Highland and Agric. Soc. of Scotland,* 1908.)

Hendriksen, *G.* Sundry geological problems. Second edition. pp. 18. Christiania 1908.

Hooper, *David.* The fats of Indian nutmegs. (From the *Agricultural Ledger,* No. 3, 1907.)

——— The seeds and oil of the Mexican poppy. (From the *Agricultural Ledger,* No. 5, 1907.)

Juritz, *Charles F.* The fertility of some colonial soils, as influenced by geological conditions. (From the *Trans. S. A. Phil. Soc.*, **18**, 1907.)

——— Analyses of grain soils. Cape division. (From the *Agric. J.*, 1908.)

——— Proportion of plant food in purple Karoo shales. (From the *Agric. J.*, 1908.)

Leather, *J. Walter.* The loss of water from soil during dry weather. (From the *Mem. Dept. Agric. India*, **1**, 1908.)

McBain, *J. W.* The experimental data of the quantitative measurements of electrolytic migration. (From the *Proc. Washington Acad. Sci.*, **9**, 1907.)

Scharff, *Ernst.* Ueber das leuchten des Phosphors und einiger seiner Verbindungen. pp. 67. Marburg 1907.

Szilard, *B.* Beiträge zur allgemeinen Kolloidchemie. pp. 42. Dresden 1908.

Wallace, *Robert.* Report on tick, redwater, or Texas fever in cattle. pp. 30. Edinburgh 1908.

LOTHAR MEYER MEMORIAL.

The Council has decided to make a donation of £10 to the Lothar Meyer Memorial Fund.

Many old pupils and admirers of the author of "Die Modernen Theorien der Chemie" may be desirous of contributing to this Memorial, and the Treasurer will be glad to receive before the end of June subscriptions from Fellows and others to the Fund.

Cheques, &c., should be made payable to Dr. Alexander Scott, crossed "Lothar Meyer Memorial Fund A/c.," and sent to the Treasurer, Chemical Society, Burlington House, W.

LIST OF FELLOWS, 1908.

The List of Fellows for 1908 is now in active preparation, and changes of address **received after 31st July cannot be included in it.**

In order that the new list may be as complete as possible, those Fellows whose degrees and Christian names do not appear in full are requested to communicate them to the Assistant Secretary.

At the next Ordinary Meeting on **Thursday**, June **18th**, 1908, at **8.30** p.m., there will be a ballot for the election of Fellows and the following papers will be communicated:

"The thermal decomposition of hydrocarbons. Part I. (Methane, ethane, ethylene, and acetylene)." By W. A. Bone and H. F. Coward.

"The rusting of iron." By W. A. Tilden.

"Studies on elementary zirconium." By E. Wedekind and S. J. Lewis.

"The constituents of Canadian hemp. Part I. Apocynin." By H. Finnemore.

"A new synthesis of apocynin." By H. Finnemore.

"The constitution of the diazonium perbromides." By F. D. Chattaway.

"Cholestenone." By C. Dorée and J. A. Gardner.

"A new form of potash bulb." By A. E. Hill.

"Solubility of silver chloride in mercuric nitrate solutions." By B. H. Buttle and J. T. Hewitt.

"The relation between absorption spectra and chemical constitution. Part IX. The nitroso- and nitro-groups." By E. C. C. Baly and C. H. Desch.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

The following Candidates have been proposed for election. A ballot will be held on Thursday, June 18th, 1908.

Ballantyne, William Henry,

99, Holmdene Avenue, Herne Hill, London, S.E.

Chartered Patent Agent and Consulting Chemist. B.Sc. (Glasgow). Fellow of the Chartered Inst. of Patent Agents. Studied Chemistry at Allan Glen's Technical School, Glasgow, 1894–97, and at Glasgow University, 1897–1900; "Joseph Black" medallist in Chemistry, 1897–98; Thomson Research Scholar, 1898–99; assisted Lord Kelvin, 1898–99, in researches on electrical properties of metals, alloys, &c.

J. A. Williamson. Robert Robertson.
Horatio Ballantyne. Frank L. Teed.
Alfred Gordon Salamon.

Bevan, Edward Morris,

10, Coronation Street, Aberkenfig.

Assistant Master responsible for the Science at the P. T. Centre, Tondû, Glam., and Lecturer in Chemistry at the Certificate Classes at Bridgend "Intermediate School." (1) Position and experience as Lecturer; (2) Inter. B.Sc., First Class, London University (Chemistry being one of the subjects of examination). Studied Practical and Theoretical Chemistry under Dr. Mills at the Northern Polytechnic, London.

W. H. Mills. S. G. Eade.
Herbert Eccles. *E. A. Tyler.*
J. M. Davey.

Blyther, Donald Francis,

77, Knights Road, Silvertown, E.

Civil Servant. Associate of the Royal College of Science, London; B.Sc. Hons., London, in Chemistry; one year in the Research Laboratory of the Royal College of Science.

William A. Tilden. G. T. Morgan.
M. O. Forster. James C. Philip.
J. T. Hewitt.

Brown, James,

20, Tower Road, Dartford, Kent.

Pharmaceutical Chemist. Manufacturing chemist with Messrs. Burroughs, Wellcome & Co., Dartford, Kent. I am desirous of keeping in touch with modern chemistry.

H. A. D. Jowett. M. Barrowcliff.
Frederic H. Lees. Francis H. Carr.
F. G. P. Remfry. Wm. C. Reynolds.

Cooper, Charles Duncan,

The Laboratory, 776, Oxford Road, Reading.

Analyst. I wish to keep in touch with recent developments of Chemistry. I am engaged at present in investigations on a technical process.

E. A. Tyler. Walter M. Gardner.
Percy Edgerton. *W. M. Seaber.*
B. North.

Cowburn, John Robert,

Belmont Villa, Birkbeck Grove, Acton, London, W.

Technical Chemist. Advanced Student in Analytical Chemistry. Certificated "Soap Making," City and London Guilds. Fourteen years' experience as Chemist and Manager in Sulphuric Acid, Alkali, and Soap Industries.

J. E. Green. John E. Farmer.
A. W. Cowburn. *William Thomson.*
T. George Shacklady. *J. Carter Bell.*

Fairweather, James Hill,

62, Wythes Road, Silvertown, E.

Analytical Chemist. I have had 5½ years' Technical training, mainly at the West Ham Municipal Technical Institute; served as Pupil Assistant to W. C. Young, F.I.C., F.C.S., Public Analyst for West Ham, Poplar, &c., and for 5 years have been his Chief Assistant.

W. C. Young. William Ping.
Harold A. Auden. W. A. Rugginz.
F. Henry Streatfeild. *George Dean.*

Falk, Kaufman George (B.Sc., Columbia; Ph.D., Strassburg),
1070, Madison Avenue, New York City.

Chemist, Columbia University. "Condensations of *o*-Phthalaldehyde" (with J. Thiele). "Ignition Temperatures of Gaseous Mixtures." "Stereochemistry of Indigo" (with J. M. Nelson). "Calculation of some Chemical Equilibria."

Frederick H. Getman. Marston Taylor Bogert.
J. Livingston R. Morgan. C. F. Chandler.
Samuel A. Tucker.

Crossley-Holland, Frank William,
Connaught Club, Marble Arch, W.

Chemist. Desires to attend the meetings of the Society; to use the Library; to keep in touch with Chemical Science.

H. A. D. Jowett. Harold C. Sayer.
F. G. P. Remfry. Francis H. Carr.
Harold Rogerson. Frederic H. Lees.

Holland, Norman,
Montreal; 4907, Sherbrooke St., W.

Superintendent, McCaskill, Dougall & Co., Varnish Manufacturers (Railway and Carriage Varnishes). Two years with Dr. J. T. Donald, Dominion Government Analyst; three years Chief Chemist, Canada Iron Furnace Co. (Blast Furnaces), Radnor Forges, Que.; one year Chemist to Riordan Pulp and Paper Co., Hawkesbury, Ont.; one and a-half years Superintendent, Vermilion Chemical Co. (Electrolytic Processes), Niagara Falls, N.Y.; three years Supt., McCaskill, Dougall & Co.

G. P. Girdwood. R. H. D. Benn.
Nevil Norton Evans. Fred. J. Hambly.
Fred. C. Dunscombe.

Hutchinson, Henry Brougham,
Ashby Villa, Devonshire Road, Harpenden.

Agricultural Bacteriologist, Rothamsted Experimental Station. Ph.D. (Göttingen). Author of "Uber Kristallbildung in Kulturen denitn. Bakterien," *Cent. Bakt. Par.*, II., B. 16, 1906; joint author of "The Cultivation of Sugar Beet in the Midlands," *Jour. Soc. Chem. Indus.*, **26**, 1907.

A. D. Hall E. J. Russell.
N. H. J. Miller. J. Golding.
Horace T. Brown.

King, James Kirkman,

55, Brewery Road, Plumstead, Kent.

Schoolmaster. B.A. (Cambridge). Natural Sci. Tripos, Part I, 1st Class; Natural Sci. Tripos, Part II (Chemistry), 2nd Class. Science Master at Dean Close School, Cheltenham, since Sept., 1905.

Arthur Hutchinson. H. J. H. Fenton.
S. Ruhemann. Isaac S. Scarf.
R. Harold C. Birt.

Lyell, Henry Robert,

"Redcott," Dacres Road, Sydenham, S.E.

Student of Chemistry. Studied at Goldsmiths' College, 1900–1906, and at King's College from 1906 to present date.

John M. Thomson. Arthur Lapworth.
Herbert Jackson. Reginald W. L. Clarke.
Patrick H. Kirkaldy. A. C. Osborn Hann.

Larmuth, Lionel Gordon,

Grove House, Cheadle Hulme, Manchester.

Manufacturing Drysalter. Attended the School of Technology, Manchester, for three years; Honours Certificate, City and Guilds; I am engaged in a Manufacturing Chemical Industry, and am desirous of keeping in touch with modern research.

W. J. Pope. J. Grant.
Jul. Hübner. F. S. Sinnatt.
L. G. Radcliffe. S. J. Peachey.

Meggitt, Alfred Ash, B.Sc. (London),

Dacca, Eastern Bengal, India.

Agricultural Chemist to the Government of Eastern Bengal and Assam, India. Studied for 4 years at the University College, Nottingham, under Profs. Clowes and Kipping. Assistant Chemist and Lecturer in Dairying, Midland College of Agric., nearly 3 years. Agric. Chemist to Govt. of Bombay, and Prof. of Agric. Chemistry, Poona, from August, 1905, to November, 1907.

John Golding. H. Sand.
J. F. Blackshaw. R. M. Caven.
Arthur Slator. F. Stanley Kipping.

Okell, Stanley Allen Warrington,

27, King's Road, Ealing, W.

Advanced Student of Chemistry at the Central Technical College (3rd year).

Henry E. Armstrong. E. Wheeler.
Edward Horton. Walter H. Glover.
William A. Davis. William Robertson.
J. Vargas Eyre.

Ray, Haradhan, M.A.,

4, Jhamapooker Lane, Calcutta.

Senior Demonstrator of Chemistry, and Analytical Chemist, Indian Association for the Cultivation of Science. M.A., 1900 (Calcutta). Sometime Professor of Physics and Chemistry, Albert College, Calcutta. At present employed as Senior Demonstrator of Chemistry, and Analytical Chemist at the above Association for the last three years.

Chuni Lal Bose. J. Sen.
T. N. Majumdar. A. L. Sircar.

P. C. Ray.

Readwin, William,

6, Kirkfield Terrace, Morley, Nr. Leeds.

Schoolmaster and Teacher of Chemistry. Teacher of the subject for upwards of twenty years; Registered Teacher of Chemistry and Physics under the West Riding County Council; Teacher of Chemistry, Cleckheaton Technical Institute.

R. H. Adie. B. North.
W. W. Tunnicliffe. Arthur Smithells.

Geo. E. Welch.

Rutter, Clement Thomas,

4, Bath Terrace, Hanwell, W.

Chemist to the Royal General Dispensary, and to the City of London Union, St. Bartholomew Close. Studied under Dr. Muter, Past President of the Society of Public Analysts. I perform all the analytical work of the Royal General Dispensary; am a Member of the Pharmaceutical Society, and desirous of keeping in touch with the latest chemical investigations.

Hermann C. T. Gardner. Robert W. Lindsey.
O. A. Elias. Sydney Dunstan.

A. H. M. Muter.

Southcombe, James Edward,

138, Chester Street, Birkenhead, Cheshire.

Chemical Research. Asst. Chemist to the Institute of Commercial Research in the Tropics; B.Sc. (1905), Liverpool; M.Sc. (1907) in Chemistry; author of "Effect of Superheated Steam on Hydrocarbon Oils," in collaboration with T. W. Worrall (*J. Soc. Chem. Ind.*, vol. xxvii, No. 7).

J. Campbell Brown. A. W. Titherley.
F. G. Donnan. Henry Bassett, jun.

Thomas Callan.

Speed, John Day,

Mill House, Enfield Lock, Middlesex.

Metallurgical Chemist. Have been employed for the past 6 years in the laboratory of the Royal Factory, Enfield Lock, as Assistant Metallurgist, the work consisting of the usual routine of analysis of steel, alloys, and general factory supplies, also the mechanical testing of same. At present time attending special course at Finsbury College under the direction of Mr. Castell-Evans, F.I.C., F.C.S.

John Castell-Evans.	*L. Dufty.*
L. H. Berry.	*E. Wheeler.*
W. R. Simpson Ladell.	*E. W. Bealey.*

Stewart, Alexander Mackintosh,

Penang, Straits Settlements.

Chemist. Did the analysis for some time in connection with the South British Marine Insurance Claims, Singapore, &c.; interested in chemical studies; partner in wholesale and retail chemists' business, Penang; Member of the Pharmaceutical Society of Great Britain.

John C. Hewlett.	*Peter MacEwan.*
Wm. Beaverly Cowie.	*William Duncan.*
E. J. Millard.	*H. H. Robins.*

Stokes, Edward,

King William's College, Isle of Man.

Schoolmaster. B.A., Adelaide, 1903; Magdalen College, Oxford, B.A., 1906; Exhibitioner, Magdalen College, 1906.

N. V. Sidgwick.	Harold Hartley.
T. S. Moore.	D. H. Nagel.

A. F. Walden.

Ward, Herbert Horace,

University College of Wales, Aberystwyth.

Analytical Chemist. For two years as Assistant to the Public Analyst for Stepney, London; twelve months Chemist in an Electrochemical Works; three years Assistant to the Lecturer on Agricultural Chemistry in the University College of Wales, Aberystwyth, and Deputy Analyst for seven counties (under the Fertilisers and Feeding Stuffs Acts) affiliated to the College.

J. J. Sudborough.	Charles A. Keane.
T. Campbell James.	H. Burrows.

Albert E. Parkes.

Wright, Charles Harold,

Government Laboratory, Port of Spain, Trinidad.

Assistant Analyst and Science Master in Trinidad (appointed March, 1908). B.A. (Cantab). Formerly Scholar of Sidney Sussex College, Cambridge; A.I.C. Assistant Master at Rivington G. S. (1902–04), at Sutton Valence School (1904–05). From Sept., 1905, to March, 1908, with Thomas Fairley, F.I.C. Author of "A Temperature Correction, &c.," *J.S.C.I.*, vol. 26, 1907 (pp. 513–5).

F. H. Neville.	Thomas Fairley.
Arthur Smithells.	B. A. Burrell.
W. Lowson.	H. L. Lee.

Yates, Harry James,

Redcroft, Four Oaks, Warwickshire.

Gas Apparatus Manufacturer (Managing Director, John Wright & Eagle Range, Ltd., Gas Stove, &c., Makers). Has made numerous investigations (still in progress) into the combustion of gas in conjunction with refractory media, and has for many years carried on chemical and other work in his own physico-chemical laboratory. Has specialised in the chemistry of gases, and is the author of a number of inventions relating to the perfecting of gas combustion. Is desirous of keeping in touch with general chemical progress.

A. T. Cocking.	Dugald Clerk.
Horatio Ballantyne.	*Harry Silvester.*
J. W. Helps.	*W. Mackean.*

Young, Charles Robert,

11, Low Pavement, Nottingham.

Demonstrator in Chemistry, University of Sheffield. B.Sc. (Lond.). Joint author with Professor Purdie, F.R.S., of "The Alkylation of Rhamnose."

William A. Tilden.	G. T. Morgan.
M. O. Forster.	Chapman Jones.
James C. Philip.	W. Palmer Wynne.

The following Certificate has been authorised by the Council under Bye-Law I (3):

Vidyant, Hari Prasad, M.A., C.E.,

Etawah, United Provinces, India.

Executive Engineer, Irrigation Branch P.W. Department. M.A.,

First Class, first on list 1894, Allahabad University; Passed as Civil Engineer, higher certificate, first on list 1897, Roorkee Thomason Civil Engineering College, India. Prizes and Medals: Gold medal, B.A., 1892, Canning College, Lucknow; Empress Victoria Jubilee medal, M.A., 1894, Allahabad University; Council of India prize of Rs. 1000 and Thomason prize of Rs. 250 (for best student); Cantley Gold medal, Mathematics; Maclaghan prize for Experimental Science (chemistry and physics). Surveying medal, Civil Engineering medal, Drawing medal, Photography medal, Roorkee. Worked at Practical Chemistry in Canning College, and also at Roorkee Engineering College. Greatly interested in Chemistry in its applications to Engineering, Agriculture, and Photography, and so desirous of keeping in touch with modern developments.

Hem Chandra Chatterji. Gopal Ch. Banerjee.

R. CLAY AND SONS, LTD., BREAD ST. HILL, E.C., AND BUNGAY, SUFFOLK.

Issued 29/6/08

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 24. **No. 344**

Thursday, June 18th, 1908, at 8.30 p.m., Sir William Ramsay, K.C.B., F.R.S., President, in the Chair.

Messrs. F. W. Caton, H. F. Coward, and E. J. Watkins were formally admitted Fellows of the Society.

The President made a short communication with reference to the Seventh International Congress of Applied Chemistry, to be held in London at Whitsuntide, 1909 (May 27th to June 2nd), under the Hon. Presidency of Sir Henry Roscoe, he himself being the acting President. The King has consented to be Patron, and the Prince of Wales Vice-Patron; it is hoped that His Royal Highness will be able to open the Congress. The meetings will be held in the University Buildings, in the Imperial College of Science, and in the Central Technical College. There are special sections for (1) Analytical Chemistry; (2) Inorganic Chemistry and Allied Industries; (3) Metallurgy and Mining—Explosives; (4) Organic Chemistry and Allied Industries; (5) Industry and Chemistry of Sugar; (6) Starch Industry; (7) Agricultural Chemistry; (8) Hygiene, Medical and Pharmaceutical Chemistry—Bromatology; (9) Photographic Chemistry; (10) Electrical and Physical Chemistry, and (11) Law, Political Economics, and Legislation with reference to Chemical Industries, of which Presidents, Vice-Presidents, and Secretaries have already been appointed.

A considerable sum has already been collected privately to meet the

expense of the Congress, and a general appeal will be issued shortly. The provisional Programme of the week has been drawn up; it comprises the opening meeting in the Albert Hall, a conversazione at the Natural History Museum, a banquet at the Crystal Palace, and lectures by Professor Haller, Professor Otto Witt, Professor Nasini, and Sir Boverton Redwood. Sectional meetings, at which papers will be read, will be held daily during the meeting. Committees have been formed in foreign countries to organise the work of the sections, and an Executive Committee has charge of the arrangements at home. It is anticipated that the Congress will be largely attended; meetings in Paris, Berlin, and Rome were attended by about 3000 chemists. The Hon. Sec. is Mr. William Macnab, of 10, Cromwell Crescent, S.W.

Certificates were read for the first time in favour of Messrs.:

William Colet Birch, B.A., 22, Glazbury Road, W. Kensington, W.

John Griffin, B.A., 7, Carlton Terrace, Batley.

Joseph Albert Hughes, School of Mines, Charters Towers, Queensland.

Thomas Ernest Hull, 6, Selborne Terrace, Greenbank, Darlington.

James Colquhoun Irvine, Ph.D., D.Sc., Dunmurry, Rathelpie, St. Andrews.

Frederick Martin Kay Menzies, M.D., F.R.C.P., 79, Davies Street, Berkeley Square, W.

Howard Houlston Morgan, B.Sc., Technical College, Auckland, New Zealand.

A Certificate has been authorised by the Council under Bye-law I (par. 3) in favour of:

H. V. Krishnayya, B.A., Mallesvaram, Bangalore, Mysore, India.

A Ballot for the election of Fellows was held, and the following were subsequently declared duly elected:

William Henry Ballantyne, B.Sc.
Edward Morris Bevan.
Donald Francis Blyther, B.Sc.
James Brown.
Charles Duncan Cooper.
John Robert Cowburn.
James Hill Fairweather.
Kaufman George Falk, B.Sc., Ph.D.
Frank William Crossley-Holland.
Norman Holland.
Henry Brougham Hutchinson, Ph.D.
James Kirkman King, B.A.
Lionel Gordon Larmuth.
Henry Robert Lyell.
Alfred Ash Meggitt, B.Sc.
Stanley Allen Warrington Okell.
Haradhan Ray, M.A.
William Readwin.
Clement Thomas Rutter.
James Edward Southcombe, M.Sc.
John Day Speed.
Alexander Mackintosh Stewart.
Edward Stokes, B.A.
Hari Prasad Vidyant, M.A.
Herbert Horace Ward.
Charles Harold Wright, B.A.
Harry James Yates.
Charles Robert Young, B.Sc.

Of the following papers, those marked * were read :—

***143. "The thermal decomposition of hydrocarbons. Part I. [Methane, ethane, ethylene, and acetylene.]" By William Arthur Bone and Hubert Frank Coward.**

The results of a systematic investigation of the modes of decomposition of the four hydrocarbons at temperatures between 500° and 1200° were described. The theories advanced by Berthelot, V. B. Lewes, and others were critically examined, and doubts raised as to the importance of acetylene as a factor in such processes.

Methane, which is by far the most stable of the four hydrocarbons, and a principal product of the decomposition of the other three, decomposes for the main part *directly* into carbon and hydrogen. The decomposition is, within the range of temperature investigated, a surface effect, and the carbon deposited is of a peculiarly hard and lustrous type. The large quantities of methane formed during the decomposition of the other three hydrocarbons can only be explained on the supposition that "residues," such as $\vdots CH$ and $:CH_2$ (which may be considered to have a momentary separate existence during the dissolution process), are directly "hydrogenised" in an atmosphere rich in hydrogen. The assumption of the momentary formation of such "residues" (or the tendency to give rise to them, which actually becomes operative at moderately high temperatures) as the result of the initial dissolution of the hydrocarbon molecule, renders it possible to formulate a rational scheme of the chief causes at work, and their modes of operation in each particular case.

It may be supposed that these "residues" are capable of (*a*) forming $H_2C{:}CH_2$ or $HC{\vdots}CH$ as the result of encounters with other like residues, or (*b*) breaking down directly into carbon and hydrogen, or (*c*) combining with hydrogen to form methane, and that all three possibilities may be realised simultaneously in proportions dependent on the temperature and the amount of hydrogen present. The scheme of decomposition of the three hydrocarbons (omitting secondary "polymeric" changes, which are essentially low temperature effects) is as follows :

$$\begin{matrix} H\,H \\ H{\cdot}\dot{C}{\cdot}\dot{C}{\cdot}H \\ \dot{H}\,\dot{H} \end{matrix} = [2(:CH_2) + H_2] = \begin{cases} (a)\ C_2H_4 + H_2. \\ (b)\ 2C + 2H_2 + H_2. \\ (c)\ \textit{plus}\ H_2 = 2CH_4 \end{cases}$$

Ethane.

$$\begin{matrix} H\,H \\ H{\cdot}\dot{C}{:}\dot{C}{\cdot}H \end{matrix} = [2(\vdots CH) + H_2] = \begin{cases} (a)\ C_2H_2 + H_2. \\ (b)\ 2C + H_2 + H_2. \\ (c)\ \textit{plus}\ 2H_2 = 2CH_4. \end{cases}$$

Ethylene.

$$\underbrace{H\cdot C{:}CH}_{\text{Acetylene}} = \underbrace{[2(:CH)]}_{\text{Polymerisation to } C_6H_6, \&c.} = \begin{cases}(b)\ 2C + H_2. \\ (c)\ \textit{plus}\ 3H_2 = 2CH_4.\end{cases}$$

Discussion.

Prof. Armstrong said that the conditions under which acetylene was produced were undoubtedly peculiar; he had sought for it in vain in the oil gas produced by cracking petroleum. If formed in the process, it underwent change very readily. It was by no means necessary to assume that the benzene which was produced was formed from acetylene. He could not agree with Dr. Bone as to the influence of surfaces in the changes studied; he thought they must play a predominant part. He was in agreement with him, however, as to the manner in which methane was formed, that is to say, that it was formed by the hydrogenation of fragments.

Dr. Divers asked whether the production of methane from acetylene at 800°, in presence of large excess of hydrogen, was not sufficiently accounted for as being the result of the union of the acetylene and hydrogen with decomposition of the product into methane, without making the assumption of the temporary existence of the substance CH?

Prof. Mills referred to the great importance of the authors' investigation, especially in connexion with the manufacture of coal gas. He thought the experiments showed that hydrogen (probably on account of its less density) protected ready-made methane better than nitrogen did. Hydrocarbons, such as CH and CH_2, if they could possibly be formed, would, in his opinion, be certain to polymerise (like acetylene, for instance), and, in their polymerised state, it would be extremely unlikely that hydrogen would combine with them.

Prof. Bone, in reply, said that he was clearly of the opinion that, whilst the decomposition of methane was, within the range of temperature investigated, entirely a surface effect, in the other three cases surface played a much less prominent part. No one, he thought, could witness the sudden decomposition of acetylene at high temperature with its accompaniment of incandescence without admitting that the chemical change took place throughout the whole mass of the gas and was not confined to the layer in contact with the hot walls of the containing vessel. Time did not permit him to cite all the evidence in favour of the hypothesis that such residues as $:CH_2$ and :CH are actually formed during these decompositions; but he thought that when Dr. Divers and Prof. Mills had had the opportunity of studying the whole of the facts brought to light during the investigation, their doubts on that point would largely disappear. He

himself felt convinced that, in the cases of ethane and ethylene, the collapse of the molecule was preceded by the elimination of hydrogen in the manner stated in the paper.

***144. "The rusting of iron." By William Augustus Tilden.**

An account was given of a series of experiments from which the following conclusions are drawn:

1. Oxygen or air together with liquid water are alone necessary to produce rusting without the assistance of carbonic acid, failure on the part of other experimenters to produce rusting in iron prepared by treatment with chromic acid being probably due to "passivity."

2. Water alone in the absence of oxygen attacks iron slowly, producing a film of what is probably ferrous hydroxide, as it is wholly converted into brown rust on admission of pure oxygen. In this connexion, the experiments of Whitney (*J. Amer. Chem. Soc.*, 1903, **25**, 298), repeated and approved by Walker, Cederholm, and Bent (*J. Amer. Chem. Soc.*, 1907, **29**, 1255), were confirmed.

3. Iron rust even when very old and constantly exposed to the weather always contains ferrous oxide.

4. The process of rusting is due in the first instance to electrolytic action promoted in all ordinary cases by the existence of carbonic acid in water exposed to the air, and by the presence in iron of various compounds of carbon, silicon, phosphorus, and sulphur. That electrolytic action does occur locally in all commercial iron, whether malleable iron, grey or white cast iron, or steel immersed in water, is shown by the use of the "ferroxyl" indicator (phenolphthalein and ferricyanide) introduced by Walker and his colleagues, and in other ways. In ordinary rusting, the process is also assisted by the depolarising action of the layer of ferric oxide or hydroxide formed externally on the rust spot.

The conditions of rusting of pure iron have never yet been studied, inasmuch as a pure iron in a massive form, if indeed in any form, is unknown.

Discussion.

Dr. Jowett said that he was interested to know that Prof. Tilden's experiments confirmed those carried out by himself many years ago. Although there were difficulties in the hydrogen peroxide theory of rusting, he would like to know how the electrolytic theory would account for the inhibiting effects of salts like sodium nitrite and potassium ferrocyanide, and the absence of this inhibiting effect by potassium nitrate and potassium ferricyanide, &c.

Prof. Armstrong said that as they were carried out in his

laboratory, he had enjoyed the opportunity of witnessing all Dr. Moody's experiments. One of his most striking observations was that a piece of iron, insulated from the glass by coating the ends with paraffin wax, had remained unrusted after many months' exposure partly immersed in water and partly in air, but, on turning the tube so that the metal came into contact with the glass at some point, the iron soon rusted. It therefore did not seem to be in a passive state. He (the speaker) thought the effect was perhaps due to silicic acid from the glass.

But even admitting, for the sake of argument, that treatment with chromic acid had rendered the iron passive, Prof. Tilden's results, important and valuable as they were, did not, in the speaker's opinion, in the least invalidate Dr. Moody's conclusions. The subject must be considered from the theoretical as well as from the practical side. Recalling the fact that, in 1885, in the course of the discussion on Mr. Brereton Baker's communication on "Combustion in Dried Gases," he had insisted that the conditions to be satisfied in the case of any chemical change were those involved in a galvanic cell—that the system must contain an electrolyte—Prof. Armstrong said that this contention had been entirely justified by later observations, especially by Mr. Baker's work on the interaction of hydrogen and oxygen. Not only was a dry mixture of these gases inert, but the presence even of liquid water was not sufficient to determine interaction; dirty water—water containing impurity which rendered it an electrolyte—alone conditioned the change. From this point of view, it was impossible that interaction should set in between iron, water and oxygen: some trace of acid impurity must be present to condition the change.

Prof. TILDEN, in reply, recalled the familiar fact that water in contact with glass became alkaline and not acid, and that, although he could not profess to account for the effects produced by all the salts mentioned by Dr. Jowett, it was obvious that all those which, like alkalis, produced hydroxyl ions in aqueous solutions would tend to retard the process of rusting.

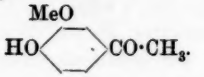
*145. "Studies on zirconium."
By Edgar Wedekind and Samuel Judd Lewis.

The authors have studied the chemical and physical properties of zirconium. From a specimen containing 95·55 per cent. of zirconium and 4·14 per cent. of oxygen, the value 14 was obtained for the atomic volume and the values 6·078 and 6·753 for the atomic heat.

146. "The constituents of Canadian hemp. Part I. Apocynin." By Horace Finnemore.

The principal constituent of the root of *Apocynum cannabinum* (0·2 per cent.) is identical with the crystalline apocynin of commerce, and with the product previously isolated by Wood (*J. Amer. Med. Assoc.*, 1904, **43**, 1953) for pharmacological purposes.

Apocynin, $C_9H_{10}O_3$, which has a faint odour of vanillin, forms slender, colourless prisms, m. p. 115°. It is convertible into a crystalline *potassium* derivative, and into *acetyl*, *benzoyl*, and *methyl* derivatives, m. p. 57°, 106°, and 51° respectively; it yields an *oxime* and a well-defined *hydrazone* and *semicarbazone*, m. p. 126° and 167° respectively; its molecule contains a single methoxyl group. As it has no aldehydic properties, it follows that apocynin is a hydroxymethoxyacetophenone. It is in fact identical with the acetovanillone (4-hydroxy-3-methoxyacetophenone) obtained by Tiemann (*Ber.*, 1891, **24**, 2855) from *iso*eugenol, and by Goldschmiedt and Hemmelmayr (*Monatsh.*, 1894, **35**, 338) from scoparin, and has the constitution (compare following abstract):



The pharmacological properties of apocynin are under investigation. A synthesis of acetovanillone from vanillic acid by Neitzel (*Ber.*, 1891, **24**, 2863) could not be confirmed, and another by T. Otto (*ibid.*) gave a yield too small for practical use; the product, however, was identical with apocynin.

147. "A new synthesis of apocynin." By Horace Finnemore.

The previously known syntheses of apocynin (acetovanillone) being unsatisfactory (preceding abstract), the author has synthesised this substance from vanillin by an application of the Grignard process. Benzoylvanillin, $C_6H_3(OBz)(OMe)\cdot CHO$, is converted by magnesium methiodide, with subsequent hydrolysis, into *benzoylapocynol*,

$$MeO\cdot C_6H_3(OBz)\cdot CH(OH)\cdot CH_3,$$

m. p. 128°, the phenolic benzoyl derivative of the secondary alcohol corresponding with apocynin. This benzoyl compound is oxidised by chromic acid mixture to *benzoylapocynin*, $MeO\cdot C_6H_3(OBz)\cdot CO\cdot CH_3$, m. p. 106°, which gives on hydrolysis 4-*hydroxy*-3-*methoxyacetophenone*, $MeO\cdot C_6H_3(OH)\cdot CO\cdot CH_3$, m. p. 115°; this is identical with natural apocynin, and with acetovanillone prepared from guaiacol (preceding abstract). The yields throughout are good.

Apocynol or 4-*hydroxy*-3-*methoxyphenylmethylcarbinol*, $MeO{\cdot}C_6H_3(OH){\cdot}CH(OH){\cdot}CH_3$, m. p. 101°, obtained by hydrolysing the above synthetic benzoyl derivative, may also be formed, although with poor yield, directly from apocynin by the action of sodium amalgam. This alcohol and the corresponding *dihydroxycarbinol*, $C_6H_3(OH)_2{\cdot}CH(OH){\cdot}CH_3$, that is formed from it by the action of suitable hydrolytic agents, promise to be of interest pharmacologically by reason of their very close relation to adrenaline.

148. "The constitution of the diazonium perbromides." By Frederick Daniel Chattaway.

The view first suggested by Kekulé as an alternative and rejected by him, that the diazonium perbromides have the constitution $R{\cdot}NBr{\cdot}NBr_2$, that is, are tri-*N*-bromo-derivatives of the hydrazines, receives strong support from the fact that they are produced quantitatively when the required amounts of bromine are added to aromatic hydrazines dissolved in acetic acid.

The author has recently shown (*Trans.*, 1898, **93**, 852) that diazonium bromides are produced quantitatively by the action of bromine on the hydrazines, and has expressed the view that these compounds when in acid solution are really di-*N*-bromo-substituted hydrazines, which are produced from the hydrazines by a process of substitution exactly similar to that which occurs when other compounds containing hydrogen attached to nitrogen are submitted to the action of bromine.

According to this view, the production of diazonium perbromides thus is the final and completing step in the replacement of the hydrogen of the $-NH{\cdot}NH_2$ group by bromine, thus:

$$\begin{matrix} R{\cdot}N{\cdot}H \\ H{\cdot}N{\cdot}H \end{matrix} \rightarrow \begin{matrix} R{\cdot}N{\cdot}H \\ H{\cdot}N{\cdot}Br \end{matrix} \rightarrow \begin{matrix} R{\cdot}N{\cdot}Br \\ H{\cdot}N{\cdot}Br \end{matrix} \rightarrow \begin{matrix} R{\cdot}N{\cdot}Br \\ Br{\cdot}N{\cdot}Br \end{matrix}.$$

The entire behaviour of the diazonium perbromides is in accord with this view of their constitution, for example, they are in exactly the condition necessary for the typical diazo-decomposition to take place; this, in fact, occurs when they are heated, suspended either in chloroform or glacial acetic acid, thus:

$$\begin{matrix} R{-}N{-}Br \\ Br{-}N{-}Br \end{matrix} \rightarrow \begin{matrix} R \\ Br \end{matrix} + \begin{matrix} N \\ \| \\ N \end{matrix} + \begin{matrix} Br \\ | \\ Br \end{matrix}.$$

All the members of the group of diazonium trihaloids have without doubt a similar constitution.

149. "Cholestenone." By Charles Dorée and John Addyman Gardner.

Cholestenone, the ketone produced by the oxidation of cholesterol under suitable conditions, reacts with ozone in chloroform solution, giving an ozonide which most probably has the formula $C_{27}H_{44}O{\cdot}O_7$. This, when decomposed by water, gives carbon dioxide and a keto-monocarboxylic acid, $C_{26}H_{42}O_3$, which is identical with the one obtained by Windaus (*Ber.*, 1906, **39**, 2008) by the oxidation of cholestenone with neutral permanganate. The work, therefore, confirms the opinion of Windaus that the double bond in cholestenone is situated in a terminal vinyl group. Cholesterol, on similar treatment, gives an ozonide, $C_{27}H_{46}O{\cdot}O_3$, which also evolves carbon dioxide on treatment with water.

Cholesterol, therefore, must possess a similar "carbon skeleton" to cholestenone, a point which had previously been regarded as doubtful.

150. "Solubility of silver chloride in mercuric nitrate solution." By Bertram Haward Buttle and John Theodore Hewitt.

The authors have studied the solubility of silver chloride in solutions of mercuric nitrate at 25°, using variable concentrations of mercuric nitrate, nitric acid, silver nitrate, and hydrochloric acid. Alteration in the concentration of the nitric acid, the other components remaining constant, has the effect of slightly increasing the precipitation of silver chloride.

From the results obtained when only the silver nitrate or hydrochloric acid is varied, the concentration of the other three components remaining unchanged, the authors arrive at the same conclusion as Morse (*Zeitsch. physikal. Chem.*, 1902, **41**, 709), that when mercuric nitrate is present in large excess, chlorine only occurs as $HgCl^{'}$ ions.

151. "The relation between absorption spectra and chemical constitution. Part IX. The nitroso- and nitro-groups." By Edward Charles Cyril Baly and Cecil Henry Desch.

The absorption spectra of compounds containing the $-NO$ and the $-NO_2$ groups have been examined. In order to guard against the disturbing influence of the benzene nucleus, the majority of compounds examined were aliphatic, several inorganic compounds being included for the sake of comparison. The results obtained show that both

groups give rise to definite selective absorption, the oscillation frequency of which, in the case of the –NO group, is strikingly low. Moreover, it is found that the nature of the atom to which the above groups are directly linked exerts a very considerable influence on the position of the band.

152. "Benzeneazo-2-pyridone." By William Hobson Mills and Sibyl T. Widdows.

An alkaline solution of 2-pyridone couples with benzenediazonium chloride to yield bright yellow *5-benzeneazo-2-pyridone* (m. p. 210—212°), the constitution of which has been established by the following synthesis. *6-Chloronicotinamide* (m. p. 210—211°) was converted by sodium hypobromite into *2-chloro-5-aminopyridine* (m. p. 82—83·5°). This reacts with nitrosobenzene to form *2-chloro-5-benzeneazopyridine* (m. p. 108—109°), which was converted by sodium methoxide into 5-benzeneazo-2-pyridone, identical with the above product.

3-Hydroxypyridine also couples in alkaline solution with benzenediazonium chloride, giving rise to *benzeneazo-3-hydroxypyridine* (m. p. 167—169°).

The preparation of *5-amino-2-pyridone*, its characterisation by its *dibenzoate*, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_5H_3N{\cdot}O{\cdot}CO{\cdot}C_6H_5$ (m. p. 211—212°), and its production together with aniline by reduction of 5-benzeneazo-2-pyridone were also described. The base was prepared in the two following ways: (1) From hydroxynicotinic acid by Curtius' method (*Ber.*, 1894, **27**, 778); ethyl hydroxynicotinate (m. p. 149—150°) is transformed through the *hydrazide* (m. p. 310°) and *azide* (m. p. 139—140°) into *bishydroxypyridylcarbamide*, $CO(NH{\cdot}C_5H_3N{\cdot}OH)_2$, which gives rise to the base on hydrolysis. (2) From the above 2-chloro-5-aminopyridine by the action of sodium methoxide.

153. "The electrolytic chlorination of the salts of some organic acids." By John Kenneth Harold Inglis and Fred Wootton.

The authors have examined the products obtained by the electrolysis of solutions containing a mixture of potassium halide with the potassium salt of an organic acid. It was found necessary to protect the liquid from the reducing action of the hydrogen by means of a porous pot. The results varied with the temperature and type of electrode employed. In the case of a solution containing potassium benzenesulphonate and potassium chloride, to which most attention has so far been paid, tri- and tetra-chloro-*p*-benzoquinone were formed

if the solution was kept hot and a platinum-foil electrode used. At the same time, evidence was obtained of the production of mono-, di-, and tri-chlorobenzenesulphonates, substitution in the nucleus having taken place. These substitution products have not yet been satisfactorily separated. In a similar manner, using potassium bromide, tetrabromo-*p*-benzoquinone was produced. A platinum-gauze electrode gave different products, which have not yet been investigated. Indefinite results were obtained with sodium benzoate, phenol, and *p*-nitrophenol. When iodide was used instead of chloride, no substitution was detected.

154. "The action of nitrous gases on di*cyclo*pentadiene." By Alexander Rule.

The author has investigated the crystalline products formed by the action of nitrous gases on a well-cooled ethereal solution of di*cyclo*-pentadiene.

The gaseous products from the action of nitric acid on arsenious oxide bring about the formation of a mixture which, on separation by means of alcohol, was found to consist of the ψ-nitrosite and the dinitro-derivative of the hydrocarbon.

The ψ-nitrosite is insoluble in cold alcohol, but on boiling is gradually dissolved, being at the same time decomposed into two molecules of nitro*iso*nitrosodi*cyclo*pentadiene. Sodium methoxide acts on the ψ-nitrosite with the formation of *iso*nitromethoxydi*cyclo*pentadiene and sodium hyponitrite. The methoxy-derivative, on treatment with nitric acid, forms a brilliant blue ψ-nitrol, which is very unstable.

The dinitro-derivative is soluble in alcohol, and thus may be easily separated from the ψ-nitrosite. It forms characteristic crystals, which melt at 121°.

Sodium hydroxide acts on the dinitro-derivative, forming *nitrohydroxydi*cyclo*pentadiene*, which also forms a characteristic, unstable blue *ψ-nitrol* with nitrous acid. The *sodium* salt of nitrohydroxydi-*cyclo*pentadiene is obtained as a crystalline mass by cooling the alkaline solution, but the free hydroxy-compound shows very little tendency to crystallise.

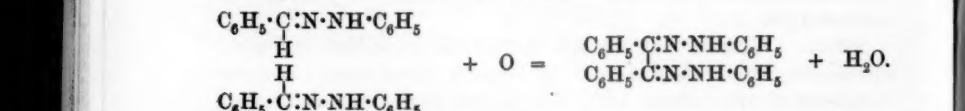
155. "An alternative structure for the supposed stereoisomeric α-osazones." By Frederick Daniel Chattaway.

By adding iodine to an ethereal solution of benzaldehydephenyl-hydrazone containing sodium ethoxide, Ingle and Mann (*Trans.*, 1895, **67**, 606) obtained two isomeric substances of the formula $C_{26}H_{22}N_4$,

melting at 186° and 208° respectively. The isomeride of lower melting point was identified with diphenyldibenzylidenehydrotetrazone, first obtained by Minunni (*Gazzetta*, 1892, **22**, ii, 217) by oxidising benzaldehydephenylhydrazone with mercuric oxide, and subsequently by von Pechmann (*Ber.*, 1893, **26**, 1045), using amyl nitrite as the oxidising agent.

Ingle and Mann made the further observation that the second isomeride, melting at 208°, was transformed into ordinary benzilosazone on heating with various solvents. Entirely on the ground that stereoisomerides of benzilosazone were required by the Hantzsch-Werner hypothesis, they assumed that their newly-discovered compound was one of these much sought for isomerides, and named it benzil-α-osazone. In order to determine its configuration, they heated both it and ordinary benzilosazone with cold concentrated sulphuric acid, and found that from the former only were they able to obtain, among other products, benzaldehyde. From this circumstance, they favoured the *syn*-configuration for the supposed new modification.

Biltz (*Annalen*, 1899, **305**, 165; **308**, 1) discovered later that Ingle and Mann's benzil-α-osazone and a whole series of similar compounds could be obtained by dissolving the corresponding hydrazones in alcohol in presence of potassium hydroxide and oxidising them by a current of air. He observed that, like the first discovered compound, all these so-called α-modifications could be transformed by heat into the corresponding β-modifications derivable directly from the diketones. Biltz offers no evidence that these new compounds are stereoisomerides of the ordinary osazones, but accepts Ingle and Mann's assumption that this is the case; indeed, he seems to regard both isomerides as formed by direct removal of hydrogen attached to carbon, and formulates the reaction thus:



Ingle and Mann in their paper record an observation which, properly interpreted, gives a far more likely explanation of this isomerism than that afforded by the Hantzsch-Werner hypothesis, and in this connexion it should be noted that in no case has the third modification of these osazones predicted by this hypothesis been obtained. They show that the diphenyldibenzylidenehydrotetrazone obtained as one of the products of their reaction undergoes intramolecular rearrangement into ordinary benzil-β-osazone on heating with alcoholic potash.

Now this isomeric change of diphenyldibenzylidenehydrazotetrazone

into benzilosazone under the influence of alcoholic potash must without doubt take place in two stages, thus:

$$\begin{matrix} C_6H_5\cdot N\cdot N{:}CH\cdot C_6H_5 \\ | \\ C_6H_5\cdot N\cdot N{:}CH\cdot C_6H_5 \end{matrix} \longrightarrow \begin{matrix} C_6H_5\cdot NH\cdot N{:}C\cdot C_6H_5 \\ | \\ C_6H_5\cdot N\cdot N{:}CH\cdot C_6H_5 \end{matrix} \longrightarrow \begin{matrix} C_6H_5\cdot NH\cdot N{:}C\cdot C_6H_5 \\ | \\ C_6H_5\cdot NH\cdot N{:}C\cdot C_6H_5 \end{matrix}$$

and, in the absence of all evidence to the contrary, Ingle and Mann's benzil-α-osazone (m. p. 208°) ought certainly to be regarded as the intermediate product of this transformation. The presence of benzaldehyde among the products of its decomposition by sulphuric acid is direct evidence in favour of this view. The author has recently shown that hydrogen attached to nitrogen in aromatic hydrazines is attacked with extraordinary readiness by free oxygen (Chattaway, *Trans.*, 1897, **91**, 1323), and his observations leave little doubt that the primary products when hydrazones are oxidised by air are hydrotetrazones, which thus undergo more or less complete transformation according to conditions. In Biltz's experiments, when the temperature is low, the first stage of transformation only occurs, the so-called α-osazones, which are really compounds of the general formula $\begin{matrix} R\cdot NH\cdot N{:}C\cdot R \\ | \\ R\cdot N\cdot N{:}CHR' \end{matrix}$, being formed; on the other hand, when the temperature is higher, the second stage of the transformation occurs and the β-compounds result, these only being true osazones of the general formula $\begin{matrix} R\cdot NH\cdot N{:}C\cdot R \\ | \\ R\cdot NH\cdot N{:}C\cdot R' \end{matrix}$.

Baly, Tuck, Marsden, and Gazdar (*Trans.*, 1907, **91**, 1579) have recently examined the absorption spectra of benzilosazone and its so-called α-isomeride. Finding them identical, they regard this as very striking and clear proof that the substances have the same configuration in solution. This appears to be a wholly unwarranted conclusion. Although such band absorptions, when different, may point to a difference of constitution, it can hardly be claimed that similarity of absorptions in such complex molecules as those in question can prove identity of configuration. To do this it would first be necessary to show that in presence of four phenyl groups a shift of one linking from nitrogen to carbon would produce an appreciable effect.

156. "The formation of 4-pyrone compounds from acetylenic acids. Part II." By Siegfried Ruhemann.

2-Phenyl-6-methyl-4-pyrone, which is formed by the action of sodium ethoxide on a mixture of acetone and ethyl phenylpropiolate (*Trans.*,

1908, **93**, 431), has been examined on lines similar to those which have been followed up by Feist (*Annalen*, 1890, **257**, 253) in his work on dimethyl-4-pyrone. Under the influence of baryta, the former compound is transformed into *benzoylacetylacetone*,

$$C_6H_5\cdot CO\cdot CH_2\cdot CO\cdot CH_2\cdot CO\cdot CH_3$$

(m. p. 106—107°). This triketone does not condense with aldehydes in the presence of piperidine or alkalis as catalysts. It reacts with two molecules of phenylhydrazine to yield a colourless *substance*, $C_{24}H_{22}N_4$ (m. p. 174—175°), which only slightly reduces Fehling's solution on boiling, and which, most probably, has the constitution $\begin{matrix}N\cdot NPh\\ \|\\ CPh\cdot CH_2\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}NPh\cdot N\\ \|\\ CH_2\cdot CMe\end{matrix}$ (see Feist, *loc. cit.*). With ammonia, the triketone condenses to form *2-phenyl-6-methyl-4-pyridone*,

$$CO\!<\!\!\begin{matrix}CH{:}CPh\\ CH{:}CMe\end{matrix}\!\!>\!NH$$

(m. p. 177—178°). This compound is characterised by the fact that its aqueous solutions readily gelatinise. Several salts of the pyridone have been prepared.

157. "The fluorescence of platinocyanides." By Leonard Angelo Levy.

Barium platinocyanide exists in two forms, which exhibit a remarkable difference in their physical properties. One variety is golden-yellow and only very slightly fluorescent, the other variety being bright green and very fluorescent. The two forms are identical in crystalline character. The yellow salt is deposited from slightly acidified solutions, whereas the green form is best obtained by crystallisation from solutions containing a trace of barium hydroxide or barium cyanide. The experiments performed lead to the conclusion that the two forms have the same chemical composition and are isomeric modifications. Similar phenomena are exhibited by the calcium salt, and to a certain extent by the cerium salt.

Barium platinocyanide, prepared from radioactive barium chloride, exhibits a strong luminosity, which is superior to that shown by a mechanical mixture of radioactive barium chloride and barium platinocyanide.

The property of fluorescence of a platinocyanide under the stimulus of radium radiations is usually exhibited in a marked degree by one hydrate form in particular. The others usually exhibit a feeble fluorescence or else show none whatever.

Certain regularities may be observed in the spectra of the fluorescence exhibited by platinocyanides of metals of the same group.

158. "The preparation of disulphides. Part II. The action of alkalis on sodium alkyl thiosulphates." By Thomas Slater Price and Douglas Frank Twiss.

The interaction between alkalis and sodium ethyl and benzyl thiosulphates in aqueous solution has been studied. The chief organic product of the action in each case is the corresponding disulphide, the main step of the reaction being probably represented by the equation :

$$R{\cdot}S_2O_3Na + NaOH = RS^- + Na_2SO_3 + -OH.$$

The RS– residues couple, in part, to give disulphide, whilst, at all events in the case of the benzyl compound, part of the RS– residues are oxidised, sodium benzyl thiosulphate giving appreciable quantities of benzoic and thiobenzoic acids.

The results were discussed in comparison with those of Gutmann (*Ber.*, 1908, **41**, 1650), who, using alcoholic solutions, has arrived at a different view of the action.

159. "Note on the formation of lead ethoxide." By Frederick Mollwo Perkin.

When thin sheets of lead are boiled in alcohol or suspended in the vapour of boiling alcohol, no action takes place, but if they are suspended over absolute alcohol and ozone is bubbled through it, in a short time the surface of the lead becomes tarnished and then assumes a brownish-yellow colour. At the end of some days, the whole of the lead is converted into a light yellow powder. On carefully washing this powder with alcohol and placing in an evacuated desiccator over sulphuric acid for some hours, a light yellow, friable powder is obtained. This, on analysis, proves to be *lead ethoxide*, $Pb(OEt)_2$. It appears to be soluble in water, although a clear solution is never obtained, probably owing to hydrolysis. It has not been found possible to obtain the ethoxide by passing oxygen alone through the alcohol, but, after the ozone has been passed for some time, the reaction can be completed by the continued passage of dry oxygen. When mercury is placed in alcohol and ozone bubbled through it, a white powder is formed which has not yet been analysed. The method is being tried with other metals.

160. "Some reactions of phenylhydrazine with metallic cyanides and other salts." By Robert de Jersey Fleming Struthers.

Phenylhydrazine in alcoholic solution combines with cuprous cyanide in ammoniacal solution to form an insoluble compound,

$2CuCN,3C_6H_5\cdot NH\cdot NH_2$. This, superficially, closely resembles the compound obtained (*Proc.*, 1905, **21**, 95) by heating cuprous cyanide in an excess of phenylhydrazine, being similarly composed of shining scales, which gradually oxidise in air and acquire a brilliant coppery sheen. These scales consist of microscopic crystals, the angles of which have now been successfully measured.

The substance readily decomposes on heating, nearly according to the equation:

$$2(2CuCN,3C_6H_5\cdot NH\cdot NH_2) = 4CuCN + 3N_2 + 3C_6H_6 + 3C_6H_5\cdot NH_2 + 3NH_3.$$

This, together with the previously described compound,

$$CuCN,C_6H_5\cdot NH\cdot NH_2,$$

co-ordinates with Moitessier's series of three compounds of phenylhydrazine with cuprous chloride, bromide, and iodide respectively (*Bull. Soc. chim.*, 1899, [iii], **21**, 666), and fills up the gaps, as below:

$2Cu_2(CN)_2,4C_6H_5\cdot N_2H_3$; $2Cu_2Cl_2,5C_6H_5\cdot N_2H_3$,
$2Cu_2(CN)_2,6C_6H_5\cdot N_2H_3$; $2Cu_2Br_2,7C_6H_5\cdot N_2H_3$,
$2Cu_2I_2,8C_6H_5\cdot N_2H_3$.

Cobalt cyanide is found to exert a powerful catalytic action on phenylhydrazine, 0·03—0·04 gram sufficing to determine the decomposition of 5 or 6 c.c. of phenylhydrazine with almost explosive violence. The mixture is heated near its boiling point for a short time until action is thoroughly established. The flame is then removed, but the action progresses with increasing intensity, and much evolution of heat, until the phenylhydrazine is completely decomposed. This catalysis by cobalt may be kept under control if only a few milligrams of the cyanide are added to 4 or 5 grams of phenylhydrazine, and the mixture distilled over paraffin, keeping the temperature carefully as low as 200°. In this way the evolved nitrogen may be easily collected and measured. The products appear to be principally aniline, benzene, ammonia, and nitrogen.

Nickel cyanide has a similar, but less, powerful action. Other salts of cobalt and nickel appear also to act more or less as catalysts. It seems possible that reduction may first occur, and the reduced metal be the true catalyst, although metallic nickel, not very finely divided, had only a slight effect. This action of cobalt is much more powerful than that of cuprous cyanide as described in the previous paper.

Other salts of copper have a strong catalytic action; cupric chloride is nearly comparable with cobalt cyanide, and finely-divided metallic copper (precipitated by iron) is fairly powerful as a catalyst. The acetate and sulphate, which deposit the metal as a mirror, are less powerful. Other metallic salts, such as lead and

bismuth, seem to exert less action. In the case of lead acetate, a mirror of lustrous and coherent lead was deposited on the glass, resembling the copper mirror obtained by Chattaway, as described by him recently.

161. "The formation of polyiodides in nitrobenzene solution. Part III. The chemical dissociation of the polyiodides of the alkali metals and ammonium radicles." By Harry Medforth Dawson.

A method has been devised by means of which the chemical dissociation in nitrobenzene solutions containing iodine and iodides of the alkali metals and substituted ammonium bases can be measured. This consists in the determination of the composition of the aqueous solutions which are in equilibrium with nitrobenzene solutions containing known quantities of iodide and iodine; from relationships which have been previously established for aqueous iodide-iodine solutions, the concentration of the free iodine in the aqueous solutions can be calculated, and from this the concentration of the free iodine in the nitrobenzene solutions is obtained.

It was shown that polyiodides of the types MI_9, MI_7, MI_5, and MI_3 exist in nitrobenzene solutions, and that these represent the successive steps in a dissociation phenomenon in which iodine is the other product of dissociation. In solutions of the same molar concentration, the polyiodides of the different alkali metals and ammonium bases are chemically dissociated to the same extent; this is probably due to the fact that the polyiodides are largely ionised, and the iodine resulting from the dissociation of a complex iodine ion which is common to the various polyiodides. Whereas the higher polyiodides are chemically dissociated to a considerable degree, the tri-iodides are very stable, and are but very slightly dissociated.

162. "The hydrolysis of amygdalin by emulsin. Part II." By Samuel James Manson Auld.

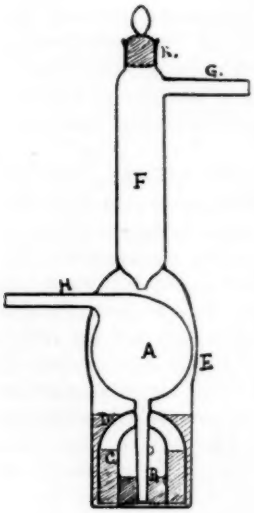
By observation of the change of rotation of the dextrose produced during the hydrolysis of mandelonitrile glucoside by emulsin and the approximate constancy of the rotation after hydrolysing amygdalin by emulsin, it is possible to show that amygdalin is derived from an $\alpha\beta$-disaccharide, the β-dextrose residue being attached to the benzaldehydecyanohydrin nucleus.

Exact measurement of the quantities of hydrocyanic acid, benzaldehyde, and dextrose formed from amygdalin shows that mandelonitrile

glucoside is formed as an intermediate product during the hydrolysis by emulsin, the biose ether-linking breaking preferentially. By stopping the hydrolysis at a suitable point, it is possible actually to isolate Fischer's glucoside.

163. "A new form of potash bulb." By Arthur Edwin Hill.

The potash bulb indicated in section in the figure consists essentially of the inlet tube *AB*, made up of the bulb *A* and its lower extension the narrow tube *B*, which extension is surrounded by, and fused to, the glass domes *C* and *D*. Enclosing these is the outer vessel *E*, to which *H*, the upper part of the inlet tube, is fused. The exit tube *F*, which is drawn off at its lower end to serve as a receptacle for holding soda-lime, is fused to the top of the vessel *E*, and provided with a ground stopper *K* and side outlet tube *G*.



To prepare the potash bulb for use, the ground stopper *K* is withdrawn, and a small plug of glass wool is inserted and pushed to the bottom of the tube *F*. Recently-ignited soda-lime, free from fine particles, is then poured into the tube until it is three parts full, and the remaining space is filled with small granules of calcium chloride; a small plug of glass wool is inserted at the top, and the ground stopper is replaced. One such filling will last for at least twenty experiments.

The bulk of the carbon dioxide is absorbed with a concentrated solution of potassium hydroxide, which is contained in the vessel *E*, and renewed after every experiment. Any residual traces of carbon dioxide are removed by the soda lime in the tube *F*, which also assists the calcium chloride to desiccate the gases before they leave the potash bulb.

A special feature of the potash bulb, which makes it very efficient, is the introduction of the domes *C* and *D*, which cause the gases to bubble through the potash solution three times in succession before they can come into contact with the soda lime in the tube *F*.

After the gases have entered the bulb *A*, they pass down the narrow tube *B*, and bubble up through the solution into the dome *C*;

they leave this through two holes in its wall, and bubble up through more solution into the outer dome *D*, which they then leave through two holes in its wall to enter the outer vessel *E*, after bubbling through the solution surrounding the dome *D*.

The position of these holes is so arranged that the gases must bubble through at least a quarter of an inch of potash solution each time; sufficient solution must be introduced into the potash bulb to cover the top of the dome *D* when the gases are bubbling through the solution. The section of the dome *D* is made elliptical in order to increase the quantity of solution adjoining the holes through which the gases bubble.

Although this bulb was designed for absorbing carbon dioxide, it can also be used for absorbing water vapour. For this purpose, the tube *F* is filled with granulated calcium chloride, and concentrated sulphuric acid is substituted for potassium hydroxide solution in the vessel *E*.

This new form of potash bulb presents a number of advantages.

(1) A treble scrubbing action, which ensures a very complete absorption by means of a comparatively small quantity of liquid absorbent, supplemented by a final scrubbing with soda-lime and calcium chloride, which also ensures complete desiccation.

(2) It is very compact and strong, being free from most of the weaknesses which characterise many of the potash bulbs now in use. It is easily manipulated, and will stand on its own base.

(3) It can be easily and rapidly wiped dry before it is weighed, and will therefore give thoroughly concordant results, which are not affected by the amount of moisture in the surrounding air.

THE LIBRARY.

The Library will be closed for Stocktaking from **Monday, August 10th**, until **Saturday, August 22nd**, 1908, inclusive.

Fellows are particularly requested to return all Library Books in their possession **not later than Wednesday, August 5th.**

LOTHAR MEYER MEMORIAL.

The Council has decided to make a donation of £10 to the Lothar Meyer Memorial Fund.

Many old pupils and admirers of the author of "Die Modernen Theorien der Chemie" may be desirous of contributing to this Memorial, and the Treasurer will be glad to receive before the end of June subscriptions from Fellows and others to the Fund.

Cheques, &c., should be made payable to Dr. Alexander Scott, crossed "Lothar Meyer Memorial Fund A/c.," and sent to the Treasurer, Chemical Society, Burlington House, W.

LIST OF FELLOWS, 1908.

The List of Fellows for 1908 is now in active preparation, and changes of address received after 31st July cannot be included in it.

In order that the new list may be as complete as possible, those Fellows whose degrees and Christian names do not appear in full are requested to communicate them to the Assistant Secretary.

The next Ordinary Meeting will be held on **Thursday**, October **22nd**, 1908, at **8.30** p.m.

R. CLAY AND SONS, LTD., BREAD ST. HILL, E.C., AND BUNGAY, SUFFOLK.

Issued 30/10/08

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 24 No. 345

The following are abstracts of papers received during the vacation and published or passed for publication in the *Transactions*:

164. "The use of the micro-balance for the determination of electrochemical equivalents and for the measurement of densities of solids." * By Otto Brill and Clare de Brereton Evans (Trans., 1908, 1442.)

By the use of the micro-balance the electrochemical equivalent of copper is found to be 31·95, and that of antimony, 40·9, the amount of metal used being from one-third to one-half of a milligram. The instrument may also be employed for determining the densities of solids which can be obtained in regular form, and thus measurable with a microscope. Results agreeing with those recorded by previous investigators were obtained by using about half a milligram of the substances selected.

165. "The preparation of disulphides. Part III. The nitrobenzyl disulphides." By Thomas Slater Price and Douglas Frank Twiss. (Trans., 1908, 1401.)

The authors have prepared o-, m-, and p-*nitrobenzyl disulphides* by the action of alkali on solutions of the corresponding nitrobenzyl thiosulphates (compare Price and Twiss, *Trans.*, 1908, **93**, 1395).

* This paper was taken as read at the meeting of May 21st, 1908.

The solution of the complex thiosulphate is obtained in each case by boiling together an aqueous solution of sodium thiosulphate and an alcoholic solution of the nitrobenzyl chloride. The most satisfactory alkali for the subsequent action is sodium carbonate. The *o*-, *m*-, and *p*-disulphides obtained melt at 109·5°, 103°, and 126·5° respectively.

166. "The relation between unsaturation and optical activity. Part III. Optically active salts of acids containing adjacent unsaturated groups." By Thomas Percy Hilditch. (Trans., 1908, 1388.)

The *brucine* and *cinchonine* salts of anthranilic and salicylic acids, and of the acetyl and benzoyl derivatives of these acids, have been prepared and measured polarimetrically, and it is found that, in general, as the number of contiguous unsaturated groups increases, the effect on the optical rotatory power of the alkaloids also increases. Further evidence has been obtained as to the effect on the optical activity of a compound when two unsaturated groups are situated at varying degrees of proximity to each other in the molecule.

167. "The constitution of glucose derivatives. Part I. Glucoseanilide, -oxime, and -hydrazone." By James Colquhoun Irvine and Robert Gilmour. (Trans., 1908, 1429.)

The behaviour of some glucose derivatives on methylation has been studied with a view to distinguishing between compounds produced from the aldehydic form of the sugar and those derived from the γ-oxidic isomerides. Glucoseanilide, when fully alkylated by the silver oxide reaction, is converted into tetramethyl glucoseanilide (m. p. 132—134°), identical in every respect with the compound previously obtained by condensing tetramethyl glucose with aniline. This result shows that glucoseanilide only contains four hydroxyl groups capable of methylation, and that the compound possesses the γ-oxidic linking characteristic of reducing sugars and glucosides. The compound should thus exist in two stereoisomeric forms (α- and β-), and evidence has been obtained that this is the case. When prepared by condensing glucose and aniline at +6°, a dextrorotatory variety is formed, which, in solution, is converted into the lævorotatory α-isomeride (α_D^{20} −52·3°), thus giving rise to extensive mutarotation. The same phenomenon has also been observed in the case of tetramethyl glucoseanilide in methyl-alcoholic solution.

Glucoseoxime behaves similarly towards the alkylating mixture of silver oxide and methyl iodide, as pentamethyl glucoseoxime was

obtained as the product of maximum methoxyl content. This compound is tetramethyl glucoseoxime methyl ether, as by hydrolysis tetramethyl glucose is produced. From this result, it is deduced that glucoseoxime, in addition to reacting as a normal oxime, is equally capable of behaving as a γ-oxide.

Similar methods when applied to glucosephenylhydrazone, led to no definite result, owing to extensive oxidation taking place.

168. "The *cis*- and *trans*-modifications of 1-methyl*cyclo*hexan-2-ol-4-carboxylic acid, and their conversion into 1-methyl-Δ^1-*cyclo*hexene-4-carboxylic acid." By Andrew Norman Meldrum and William Henry Perkin, jun. (Trans., 1908, 1416.)

The authors have reduced 2-hydroxy-*p*-toluic acid by sodium and alcohol, and find that the product of reduction is readily converted into 1-*methyl*-Δ^1-cyclo*hexene*-4-*carboxylic acid*.

$$CMe\begin{matrix}<CH-CH_2\\ CH_2\cdot CH_2\end{matrix}>CH\cdot CO_2H,$$

by treatment first with hydrobromic acid and then with diethylaniline.

169. "Studies on the viscosity and conductivities of some aqueous solutions. Part I. Solutions of sucrose, hydrogen chloride, and lithium chloride." By W. Heber Green.

The viscosity of sucrose solutions at 18° and 25°, the viscosity and conductivity of hydrochloric acid at 25°, and of lithium chloride solutions at 18° and 25°, have been measured over ranges of concentration limited only by the solubilities of each substance.

The densities of lithium chloride solutions have been re-determined and compared with the results obtained by previous observers.

The viscosity results obtained show that various formulæ which have been suggested do not at all accurately represent the connexion between viscosity and concentration, especially when concentrated solutions are examined. The most concordant result was obtained by using an expression of the form $\eta/\eta_0 = A^{v/w}$, where v = volume of solute, and w = volume of solvent, present per unit-volume of solution.

170. "Studies on the viscosity and conductivity of some aqueous solutions. Part II. Mixtures of solutions of sucrose and lithium chloride; a contribution towards the elucidation of the connexion between ionic mobility and the fluidity of the solution." By W. Heber Green.

The conductivity and viscosity of aqueous solutions have been measured at 25° of three series of mixtures of lithium chloride and

sucrose, in which the ratio of the number of lithium chloride molecules to the number of sucrose molecules was 1 : 0·2, 1 : 2·0, and 1 : 20 respectively.

By extrapolation from the results for these mixtures the conductivity and viscosity values have been calculated for a series in which the above ratio was $1 : \infty$. In this way the variations in the ionic mobilities at infinite dilution of the salt, concomitant with change of fluidity due to the presence of sugar in solution, were rendered free from some, if not all, disturbing factors.

The curves obtained show that the ionic mobility is not simply proportional to the physical fluidity of the solution, but more nearly to the two-thirds power in the case of lithium chloride and sucrose; with other ions, and other molecules giving rise to viscosity, the exact function varies, and presumably depends on the relative molecular sizes.

With reference to Hartley, Thomas, and Applebey's use of pyridine as an agent for producing viscosity, the author maintains that Stokes' theorem does not hold for a body of molecular size migrating through a medium composed of bodies comparable in size to itself, and, further, that there is no direct evidence for the presence of an aqueous envelope permanently attached to each ion.

No trustworthy method has as yet been established whereby the true ionisation coefficients of a salt can be determined except in solutions of extreme dilution.

171. "The reduction of refractory oxides by carbon."

By Harold Cecil Greenwood. (Trans., 1908, 1483.)

A method has been devised for measuring with an accuracy of about $\pm 10°$ the temperatures of reduction of oxides by carbon, the apparatus being suitable for use up to at least 2000°. The reduction temperatures of the oxides of chromium, manganese, uranium, silicon, tungsten, zirconium, and thorium have been measured, and are all found to be far below those previously estimated.

Commencement of the reaction occurs sharply, but the progress of the reduction depends greatly on the intimacy of admixture. The nature of the carbon employed, as also the physical condition of the oxide, exerts a marked influence on the temperature of reduction.

The reactions, so far as the oxides mentioned above are concerned, are found to occur directly between the carbon and the oxide, and are not due to thermal dissociation.

172. "The production of ferro-alloys."
By Harold Cecil Greenwood. (Trans., 1908, 1496.)

This investigation is an extension of the work described in the preceding paper. In the case of some of the oxides studied, for example, silica and manganous oxide, it is found that a "catalytic" facilitation of the reduction takes place when metals such as iron, manganese, and copper are present. This confirms observations made in the technical preparation of ferro-alloys under conditions which are unsuitable for the isolation of the pure metal. The lowering of the reduction temperature appears to be due to mutual chemical affinity of the two metals, and also in some cases to the alloy being more fusible than the refractory metal; no evidence is forthcoming to show that reduction is assisted by the heat of reaction of ferric oxide and carbon when this oxide is added instead of metallic iron.

173. "The rapid electroanalytical deposition and separation of metals. Part II. Antimony and tin. The employment of a diaphragm." By Henry Julius Salomon Sand.
(Trans., 1908, 1572.)

By means of the apparatus already described, antimony has been estimated in sulphuric acid solutions and suspensions in the presence of hydrazine sulphate, and also in solutions containing chlorides. A high temperature is maintained, and the potential of the cathode is kept under control.

Tin has been deposited from stannic solutions containing a small amount of free sulphuric acid and a sufficiency of oxalic acid at a temperature near the boiling point.

Antimony has been separated from tin. Any *b*-stannic acid which may be present must first be converted into the *a*-form. The electrolyte consists of equal volumes of sulphuric acid and water; a small amount of hydrazine sulphate is added, and the temperature maintained at a little above 100°. The maximum auxiliary voltage is 0·65.

The tin is determined electrolytically in the remaining liquid after neutralisation with ammonia and the addition of oxalic acid. After the greater part of the metal has been deposited, it is necessary to add hydrochloric acid and hydroxylamine hydrochloride in order that the electrolyte may be exhausted; a high temperature is maintained. A considerable number of analyses have been carried out in which the combined metals, taken in varying ratios, weighed approximately one gram. The time for the deposition of the antimony was usually about twenty minutes, and that for the tin about eighty minutes.

An apparatus which allows the employment of a diaphragm in rapid electroanalysis has been constructed, and tested in the determination of copper and its separation from iron.

174. "The measurement of a homogeneous chemical change in a gas. (The thermal decomposition of ozone.)" By Herbert Edmund Clarke and David Leonard Chapman.

(Trans., 1908, 1638.)

It has been commonly supposed that slow pyrogenic changes in gases have their seat principally, if not entirely, on the walls of the enclosing vessel. The authors have succeeded in demonstrating that this conclusion is not true in the case of the decomposition of ozone. In vessels of German glass, of which the ratio of surface to volume is not too large, the rate of decomposition of ozone at 100° is independent of the area of the surface of the globe, a fact which proves that the change is a homogeneous one.

175. "The proteins of egg-yolk." By Robert Henry Aders Plimmer.

(Trans., 1908, 1500.)

In addition to the protein, vitellin, which contains one per cent. of phosphorus and which is insoluble in water, egg-yolk contains a second protein, which contains 0·1 per cent. of phosphorus and which is soluble in water and coagulable by heat.

It can be prepared either by extracting the yolks, after treatment with ether, with a large volume of water and heating to boiling in the presence of a small quantity of acetic acid, or by boiling the water used for precipitating the vitellin; this is obtained by dissolving the yolk in 10 per cent. sodium chloride solution, extracting with ether, and precipitating with 20 volumes of water. The second method gives a purer preparation of this protein.

This protein differs from ovalbumin in its content of nitrogen as also in the amounts of the various nitrogen constituents contained in it when determined by Hausmann's method, so that it is not identical with this protein; its behaviour towards ether also indicates this. The various amounts in which the nitrogen constituents are present in the protein are very similar to those in vitellin, and suggests a close relationship between these proteins in egg-yolk; hence the name of *livetin* is suggested for this new protein.

176. "The conductivities of the α-oximino-fatty acids." By John Kenneth Harold Inglis and Lottie Emily Knight. (Trans., 1908, 1595.)

The authors have prepared specimens of the first four of these acids by the action of nitrosulphonic acid on acetoacetic ester and its derivatives. The conductivities agree fairly closely with those measured by Hantzsch and Miolati. Measurements of the conductivities of the sodium salts and comparison of the acids with one another have indicated that the acids are not all of the same configuration, but that oximinopropionic acid is different from the others. The authors have also found evidence of the existence of two forms of α-oximinobutyric and -valeric acids.

177. "Studies of the perhalogen salts. Part II." By Charles Kenneth Tinkler. (Trans., 1908, 1611.)

The formation of periodides has been further investigated by means of the ultra-violet absorption spectra of solutions of iodine containing a halogen salt. The iodine additive compounds of trimethylsulphine iodide, bromide, and chloride, which may be either (I) $(CH_3)_3\overset{(IV)}{S}X{\cdot}I_2$ or (II) $(CH_3)_3\overset{(VI)}{S}\begin{matrix}X\\ I\\ I\end{matrix}$ (X = I, Br, or Cl), gave spectra which are identical with those of solutions of iodine containing potassium iodide, bromide, and chloride respectively. This agreement shows that these substances contain the true perhalogen groups, and affords evidence in favour of formula I.

The formation of perbromides (by the addition of a bromide to bromine water) has also been investigated by the spectroscopic method, and evidence obtained of the existence of these substances in a large number of cases. Evidence was also obtained of the formation of bromine additive compounds of chlorides.

178. "The formation of ethers from compounds of the benzoin type." By James Colquhoun Irvine and David McNicoll. (Trans., 1908, 1601.)

The authors find that the methyl ethers of benzoin should always be prepared by the silver oxide reaction, as by the use of Fischer's process of methylation the yields obtained are poorer, and in some instances furan derivatives are formed in quantity. In the case of anisoin, no

methyl ether is produced in the latter reaction, which gives rise to the *tetramethoxyl* derivatives of α-methoxy-αβ-dibenzoyldibenzyl (m. p. 218—219°) and of 2-hydroxy-3 : 5-dimethoxytetraphenyltetrahydrofuran (m. p. 263—265°).

The hydrochloric acid method can also be applied to *o*-dimethoxybenzoin only within a limited range of concentration of the acid, as the benzoin readily undergoes molecular rupture to give *o*-methoxybenzoic acid. When the same process is applied to furoin, no methylation takes place, condensation products containing five furyl residues and analogous to those obtained from ordinary benzoin being produced. On the other hand, ethyl ethers of benzoins are comparatively readily prepared by Fischer's method, and no furan derivatives are formed.

In the course of the work, several benzoin ethers have been prepared by the silver oxide method, and the compound described by Limpricht and Jena as "ethyl benzoin" has been examined and shown to be a mixture of hydrobenzoin and *iso*hydrobenzoin.

179. "Aromatic α-disulphones." By Thomas Percy Hilditch. (Trans., 1908, 1520.)

Aromatic α-disulphones, previously obtained only by the interaction of an aromatic sulphonyl chloride and the sodium salt of an aromatic sulphinic acid, have been prepared in yields varying from 17 to 40 per cent. by the oxidation of sulphinic acids by potassium permanganate in glacial acetic acid solution. *Diphenyl*, *di*-p-*phenetyl*, *di*-p-*tolyl*, and *di*-p-*xylyl* *α-disulphones* have been thus obtained as well-crystallised, stable substances of high melting point; they are decomposed slowly by strong ammonia into a mixture of sulphonamide and sulphinate, and by warm aqueous potassium hydroxide into the corresponding sulphonates and sulphinates.

180. "The action of bromine on β-hydrindone." By Norman Allen Creeth and Jocelyn Field Thorpe. (Trans., 1908, 1507.)

The bromination of β-hydrindone may be effected by the action of bromine in chloroform solution, all four hydrogen atoms of the hydrindene ring being replaced by the halogen. A *monobromo*- and a *dibromo*-derivative may also be prepared by using the calculated quantity of bromine, but ααγ-tribromo-β-hydrindone cannot be produced in this way, since, when the amount of bromine required for its formation is employed, an equimolecular mixture of αγ-dibromo-β-hydrindone and *ααγγ-tetrabromo-β-hydrindone* is alone formed. The monobromo- and dibromo-derivatives are neutral substances insoluble

in alkalis, showing, therefore, that the combination of the halogen with the α-carbon atom of β-hydrindone does not transform the compound into a derivative of hydroxyindene. The action of alkalis on the various bromo-derivatives has been investigated, but only in the case of $\alpha\alpha\gamma\gamma$-tetrabromo-β-hydrindone has a well-defined product been obtained. In this instance, through a curious fission of the hydrindene ring, the product consists of phthalidecarboxylic acid.

181. "On polymorphism, with especial reference to sodium nitrate and calcium carbonate." By William Barlow and William Jackson Pope. (Trans., 1908, 1528.)

In continuation of their previous work, the authors discuss the relation between the crystalline form and the chemical constitution exhibited in connexion with a number of well-known cases of polymorphism.

182. "The oxidation of phosphorous acid by iodine." By Bertram Dillon Steele.

In continuation of the investigation of the reaction between iodine and hypophosphorous acid, the velocity of interaction of iodine and phosphorous acid has been studied. It has been found that two reactions of essentially different character occur between these reagents, one of which preponderates in more strongly acid solution, and the other, in the presence of feeble acids, such as acetic and boric acids.

The former of these reactions is catalytically accelerated by the presence of hydrogen ions, and the velocity is proportional to the concentration of phosphorous acid (or of the phosphorous ion) and to the square root of the concentration of the iodine.

The conclusion is drawn that reaction takes place between phosphorous acid molecules (or ions) and iodine atoms, the latter being supplied in extremely small, but sufficient, quantity by the dissociation of the iodine molecules. A slight apparent retardation of the reaction velocity by the iodine is probably due to the incompleteness of the hypothesis which has been suggested to explain the experimental results.

The second reaction, which occurs in the presence of salts, such as sodium acetate, bicarbonate, or biborate, is so complex that the attempt to formulate a hypothesis explanatory of the reaction has been abandoned. The reaction is accelerated by the presence of phosphorous acid and of sodium acetate, and retarded by the presence of iodine and of potassium iodide.

183. "The direct interaction of magnesium and alkyl halides." By James Frederick Spencer and Mary S. Crewdson.

It has been found that all alkyl halides react directly with magnesium. The halides of hydrocarbons lower in the series than butane only react when heated in a sealed tube, but, with the exception of the chlorides, which, so far as has been investigated, appear always to require heating in a sealed tube, all the halides of hydrocarbons higher in the series than butane react with magnesium when the two substances are heated together in a flask. The products are magnesium alkyl halides and hydrocarbons containing twice as many carbon atoms as the original halide. In the reactions taking place in sealed tubes, unsaturated hydrocarbons, of both the acetylene and the olefine series, together with much hydrogen, are also found, in addition to the above-mentioned compounds. Methyl bromoacetate also reacts directly with magnesium, giving good yields of methyl acetate and dimethyl succinate, and aromatic chloro-derivatives react with magnesium when heated with it in a sealed tube, yielding the corresponding hydrocarbons in good yield.

184. "The interaction of the metals of the aluminium group and organic halogen derivatives." By James Frederick Spencer and Marion L. Wallace.

Aluminium, indium, and thallium react directly with both aromatic and aliphatic halogen derivatives on heating. In the case of the chloro-derivatives and the lower aliphatic compounds (up to butane), heating in a sealed tube was necessary to bring about the reaction. The formation of an intermediate aluminium organic halide, similar to the Grignard compounds, is the primary result of this interaction, and this compound is decomposed on the addition of water with the production of the parent hydrocarbon and the evolution of much heat. In some cases, the evolution of heat does not take place, and in these cases the parent hydrocarbon is present in the mixture before the addition of water. In all such cases the reactions are extremely slow, it being necessary to heat the substances for twenty-four to thirty hours before the reaction is complete ; so that in all probability the intermediate compound is formed and then decomposed by the atmospheric moisture. The indium and thallium reactions, of which only few have been studied, proceed very slowly, as, indeed, do also some of the aluminium reactions, but certain of the latter take place with extreme violence. The yield of hydrocarbons varies

from 25 to 75 per cent. of the theoretical. In a few cases, the reaction proceeds along a second line, namely, the formation of a hydrocarbon or derivative containing double the number of carbon atoms as the original substance. The best examples of this are the formation of dimethyl succinate from methyl bromoacetate, and the formation of benzidine from bromoaniline by the action of aluminium. In no case could a reaction between these metals and the halide derivatives be brought about in ethereal solution.

185. "The relation between unsaturation and optical activity. Part IV. The relative influence of bi-, quadri-, and sexavalent sulphur on rotatory power." By Thomas Percy Hilditch. (Trans., 1908, 1618.)

The optical activity of derivatives of *l*-amyl alcohol and *d*-camphor containing sulphur of all the above degrees of valency has been compared, and it has been found that a bi- or quadri-valent sulphur atom has a larger effect on optical rotatory power than saturated sexavalent sulphur, and, also, that the optical anomaly is enhanced by the presence of a second unsaturated group adjacent to the sulphur residue. The maximum change of rotatory power appears to take place when two identical unsaturated groups occur in conjugation, as in the disulphides.

In addition, the study of a series of active salts of corresponding sulphinic and sulphonic acids shows that the sulphonic acid exerts a greater influence on the rotatory power of the base, and this agrees with the effect of unsaturation observed in other cases, on the assumption that the sulphinic salts contain sexavalent sulphur.

186. "Oxidations of hydrocarbons of the benzene series. Part II. Substances containing a negative radicle." By Herbert Drake Law and Frederick Mollwo Perkin. (Trans., 1908, 1633.)

The authors have investigated the oxidation of the nitrotoluenes with chromyl dichloride. Contrary to Étard's statement that quinones are produced, *p*- and *m*-nitrotoluene give good yields of the corresponding aldehydes. With *o*-nitrotoluene, no aldehyde is formed, but a chlorinated compound of no definite boiling point. With *o*-, *m*-, and *p*-chlorotoluenes, the corresponding aldehydes are in all cases obtained. Diphenylmethane yields diphenylcarbinol, and triphenylmethane gives triphenylcarbinol; in both cases in practically theoretical yields. Naphthalene, anthracene, and fluorene were also oxidised, but definite products were not obtained.

187. "Coprosterol. Part I."
By Charles Dorée and John Addyman Gardner. (Trans., 1908, 1625.)

Having shown that cats and dogs when fed on a raw brain diet produce coprosterol in considerable amount, the authors have studied the action of oxidising and isomerising agents on the substance. Coprosterol is readily oxidised by chromic acid to a ketone, *coprostanone*, which crystallises in leaves melting at 62—63°. The *semicarbazone* melts at 192°, and the *oxime* at 69°. Coprostanone forms with phenylhydrazine a crystalline substance melting at 191°, to which a formula has not yet been assigned. When heated with sodium amyloxide, coprosterol is converted into *ψ-coprostero'*, melting at 119°, and yielding an *acetate*, m. p. 83°, and a *benzoate*, m p. 85°, which differ from the corresponding derivatives of coprosterol. On oxidation with chromic acid, however, it yields the same ketone, coprostanone.

188. "The spontaneous crystallisation of solutions of some alkali nitrates." **By Bernard Mouat Jones.** (Trans., 1908, 1739.)

The author has determined the temperatures of spontaneous crystallisation of supersaturated solutions of the nitrates of potassium, rubidium, and cæsium of various strengths. The method was that used by Hartley, Jones, and Hutchinson (*Trans.*, 1908, **93**, 825) in investigating sodium sulphate solutions. The effect of mechanical friction was studied by introducing fragments of Jena glass into the tubes before sealing. Crystalline fragments, such as garnet, were not used, in order to avoid possible unequal "inoculating" effects on the three solutions. The temperatures at which supersaturated solutions of the salts in question would crystallise spontaneously when slowly cooled and constantly shaken have been recorded. Temperatures corresponding with tubes containing glass fragments lie on regular curves, namely, the supersolubility curves, above which crystallisation cannot take place in the absence of crystal nuclei. Tubes containing no glass fragments generally needed to be cooled into the labile region before crystallisation would occur. The supersolubility curves for potassium and rubidium nitrates run nearly parallel to the solubility curves, approaching the latter as the concentration decreases. For cæsium nitrate, the solubility and supersolubility curves coincide, the metastable region disappearing.

The three corresponding ice-supersolubility curves have been traced, and also the ice-solubility curves for dilute solutions of rubidium and cæsium nitrates. The spontaneous production of the ice phase

seems to be a somewhat less definite phenomenon than the production of the salt phase.

Although the order of molecular solubility is rubidium nitrate, potassium nitrate, cæsium nitrate, the order for the sizes of the metastable ranges follows that of the molecular weights, that for potassium nitrate being greatest, and that for cæsium nitrate least. For example, for a concentration of 0·6 gram-mols. of salt to 100 grams of water, the metastable ranges are approximately 4°, 1°, and 0° respectively.

189. "Syntheses with phenol derivatives containing a mobile nitro-group. Part I. The interaction of 2 : 3 : 5-trinitro-4-acetylaminophenol and amines." By Raphael Meldola and James Gordon Hay. (Trans., 1908, 1659.)

The trinitroacetylaminophenol referred to was described by one of the authors in 1906 (*Trans.*, **89**, 1935), and its great reactivity, due to the mobility of the 3-nitro-group, indicated in that paper. The compound has now been submitted to further investigation, more especially with reference to the formation of iminazoles from amines. In the present paper, the authors consider the mechanism of the formation of iminazoles in connexion with the conditions that determine the mobility of the nitro-group on the one hand, and, on the other, the nature of the amine with which the trinitro-compound is brought into combination. A quantitative method for determining the yield of iminazole has been devised, and complete series of determinations have been carried out with the isomeric chloroanilines, nitroanilines, and anisidines. The results bring out very clearly the influence of steric hindrance in the case of ortho-substituted amines, the nitro-group being so completely protective that no combination takes place with *o*-nitroaniline. Other series of isomerides are under investigation, and also the products of condensation of secondary amines; dimethylamine and piperidine having been found to react readily, whilst no combination takes place with methylaniline, benzylaniline, diphenylamine, or carbazole. A number of new iminazoles have been prepared, and are described in the paper.

190. "The constituents of the expressed oil of nutmeg." By Frederick Belding Power and Arthur Henry Salway. (Trans., 1908, 1653.)

Ceylon nutmegs, of good quality, yielded on expression 26·6 per cent. of oil, and when completely extracted with ether, 42·9 per cent.

of oil was obtained. The constants of the expressed oil and of the total fatty acids were as follows:

	Expressed oil.	Total fatty acids.
Melting point	48°	49°
Density, 50°/50°	0·9399	0·9012
Acid value	11·2	218·3
Saponification value	174·6	—
Iodine value	57·8	23·1

The composition of the expressed oil or fat was approximately as follows: Essential oil (12·5 per cent.); trimyristin (73·0 per cent.); oleic acid, as glyceride (3·0 per cent.); linolenic acid, as glyceride (0·5 per cent.); formic, acetic, and cerotic acids (very small amounts); unsaponifiable constituents (8·5 per cent.); resinous material (2·0 per cent.).

The chief unsaponifiable constituent was a new *compound*, $C_{18}H_{22}O_5$, amounting to about 5 per cent. of the expressed oil. It is a yellow, transparent, extremely viscid liquid (b. p. 270—280°/15 mm.), and is devoid of any marked physiological action. The remainder of the unsaponifiable material consisted of myristicin, $C_{11}H_{12}O_3$, with a little phytosterol, $C_{20}H_{34}O$ (m. p. 134—135°).

191. "The preparation of disulphides. Part IV. Esters of dithiodiglycollic and dithiodilactylic acids." By Thomas Slater Price and Douglas Frank Twiss. (Trans., 1908, 1645.)

On submitting the mixture obtained by the interaction of ethyl bromoacetate and sodium thiosulphate in aqueous-alcoholic solution to electrolysis in the cathode compartment of a divided cell, diethyl dithiodiglycollate separates as a heavy oil; from methyl bromoacetate the dimethyl ester is obtained. In a similar manner, the diethyl esters of α-dithio- and β-dithio-dilactylic acids were prepared from ethyl α-bromopropionate and ethyl β-iodopropionate respectively. These esters are all fairly mobile liquids, heavier than water, and possessing a peculiar odour which is not very disagreeable, and not at all like that which is usually associated with the liquid mercaptans and disulphides. The boiling points of these esters are as follows: *dimethyl dithiodiglycollate*, 154°/14 mm.; *diethyl dithiodiglycollate*, 164°/14 mm.; *diethyl α-dithiodilactylate*, 159°/14 mm.; *diethyl β-dithiodilactylate*, 194°/17 mm.

For complete identification of these esters, the corresponding acids were prepared from them by hydrolysis with hydrochloric acid. The properties of the acids obtained agreed with those found by previous observers.

192. "Contributions to the chemistry of the cholesterol group. Part I. The action of hydrogen peroxide and of fused potassium hydroxide on cholesterol." By Robert Howson Pickard and Joseph Yates. (Trans., 1908, 1678.)

A detailed account of work, of which a preliminary account has already appeared (this vol., 121).

193. "Derivatives of *S*-phenylphenazothionium. Part II." By Samuel Smiles and Thomas Percy Hilditch. (Trans., 1908, 1687.)

Further proof of the constitution of these substances is now offered from a general standpoint. Condensation of phenol with di-*p*-nitrodiphenylamine sulphoxide yields the sulphates of two isomeric *S*-hydroxyphenylphenazothionium bases, which are distinguished by their different solubilities and colours in various media. The reduction products of the dinitro-*S*-phenetyl and -hydroxyphenyl derivatives have also been prepared; these on oxidation yield blue dyestuffs similar to thionine. *iso*Dinitrodiphenylamine sulphoxide yields similar derivatives, which are distinguished from those of the di-*p*-nitro-series by greater solubility and absence of fluorescence.

194. "The trithionates and tetrathionates of the alkali metals. Part I." By John Edwin Mackenzie and Hugh Marshall. (Trans., 1908, 1726.)

The authors have prepared a number of tetrathionates from persulphates and thiosulphates (compare Marshall, *J. Soc. Chem. Ind.*, 1897, **16**, 396), thus: $2SrS_2O_8 + K_2S_2O_8 = K_2S_4O_6 + 2SrSO_4$, and of trithionates by removal of sulphur, thus: $K_2S_4O_6 + K_2SO_3 = K_2S_3O_6 + K_2S_2O_3$. The crystallographic details of some of the salts are as follows:

Potassium trithionate, $K_2S_3O_6$. Rhombic, bipyramidal. $a:b:c = 0{\cdot}7168:1:0{\cdot}4193$. Refractive indices: $\alpha = 1{\cdot}4925$, $\beta = 1{\cdot}5646$, $\gamma = 1{\cdot}6014$. Calculated axial angle, $2V = 68°15'$. Density, 2·336. Molecular volume, 115·8.

Rubidium trithionate, $Rb_2S_3O_6$; isomorphous with the above. $a:b:c = 0{\cdot}7058:1:1{\cdot}04176$. Refractive indices: $\alpha = 1{\cdot}4874$, $\beta = 1{\cdot}5580$, $\gamma = 1{\cdot}5867$. Calculated axial angle, $2V = 62°23'$. Density, 2·845. Molecular volume, 127·7.

Caesium trithionate, $Cs_2S_3O_6$, is not isomorphous with the above. Triclinic. Density greater than 3·326.

Cæsium trithionate monohydrate, $Cs_2S_3O_6,H_2O$. Triclinic. Density, 3·192. Molecular volume, 149·1.

The authors find that rubidium and cæsium can be estimated by conversion into the double sulphate of calcium and the alkali metal.

195. "The synthesis of complex acridines." By Percy Corlett Austin. (Trans., 1908, 1760.)

The author has applied the methods employed by Senier and himself in the synthesis of various phenonaphthacridines and dinaphthacridines (*Trans.*, 1906, **89**, 1387; 1907, **91**, 1233, 1240; 1908, **93**, 63) to the synthesis of acridines derived from phenanthrene and the closely-allied fluorene. A phenophenanthracridine has also been prepared by the condensation of phenanthraquinone and *o*-nitrobenzyl chloride in the presence of stannous chloride. This is an adaptation of Baezner's reaction (*Ber.*, 1904, **37**, 3077).

Diphenanthracridine, $C_{14}H_8<\begin{matrix}N\\|\\CH\end{matrix}>C_{14}H_8$, is a yellow, crystalline substance, insoluble in most solvents; it can be distilled under diminished pressure, and recrystallised from nitrobenzene. Its melting point is above 320°.

Phenophenanthracridine, $C_{14}H_8<\begin{matrix}N\\|\\CH\end{matrix}>C_6H_4$, is prepared by treating an alcoholic solution of a mixture of phenanthraquinone and stannous chloride with *o*-nitrobenzyl chloride. After distillation under diminished pressure, it crystallises from benzene in yellow crystals, melting at 204°.

Fluorene-$\begin{matrix}N\text{-}\alpha\\|\\CH\text{-}\beta\end{matrix}$*-naphthacridine*, $C_{13}H_8<\begin{matrix}N\\|\\CH\end{matrix}>C_{10}H_6$, is prepared from 2-aminofluorene and α-naphthol by the action of methylene di-iodide. After distillation under diminished pressure and recrystallisation from toluene, it melts at 259°.

A brown powder is also obtained by the action of methylene di-iodide on 2-aminofluorene, but no method was found for the purification of this substance.

196. "A reaction distinguishing phosphoprotein from nucleoprotein, and the distribution of phosphoproteins in tissues." By Robert Henry Aders Plimmer and Frederick Hughes Scott. (Trans., 1908, 1699.)

In 1906, Plimmer and Bayliss (*J. Physiol*, **33**, 439) found that the phosphorus of caseinogen was completely eliminated as phosphoric acid

by the action of one per cent. aqueous sodium hydroxide at 37° in twenty-four hours.

The phosphorus of vitellin, the other well-defined phosphoprotein, is eliminated as phosphoric acid under the same conditions, but the phosphorus of nucleic acid, lecithin, and glycerophosphoric acid, the other phosphorus-containing substances in the tissues, is not separated in this way.

The reaction thus serves as a simple means of distinguishing phosphoproteins from nucleoproteins, and it permits of the determination of the presence of phosphoproteins which are stated to occur in various tissues.

As phosphates are present in all tissues, the reaction cannot be applied directly, but by first extracting the fats and lecithin with alcohol and ether, dissolving out the phosphates from the coagulated protein with water acidified with hydrochloric acid, and then treating it with one per cent. aqueous sodium hydroxide at 37°, the presence of phosphoprotein can be demonstrated. By this procedure, a determination of the amount of the various kinds of phosphorus compounds in the tissues can also be made.

The pancreas alone of the tissues examined contained phosphoprotein, the amount of phosphorus present in this form being about 3 per cent. of the total phosphorus.

Ichthulin, the protein contained in caviar, the eggs of the sturgeon, is described as a phosphoprotein. Its nature has been confirmed by this method, and phosphoproteins have also been found in the eggs of the herring and mullet.

The principal distribution of phosphoproteins is thus in those substances which form the food-stuffs of the embryo bird and fish and the young mammal.

197. "The colouring matters of the stilbene group. Part V. The action of caustic alkalis on derivatives of para-nitrotoluene." By Arthur George Green and James Baddiley. (Trans., 1908, 1721.)

Derivatives of *p*-nitrotoluene containing as ortho-substituent electropositive or weakly electronegative groups (CH_3, OMe, or CO_2H), react least readily with caustic alkalis, giving red intermediate compounds, and on oxidation, derivatives of dinitrodibenzyl. By carrying the combined condensation and oxidation further, the dinitrodibenzyl derivatives are finally converted into dinitrostilbene derivatives, apparently by intermediate formation of nitronitrosostilbenes:

$$\begin{matrix} CH_2\cdot C_6H_4\cdot NO_2 \\ | \\ CH_2\cdot C_6H_4\cdot NO_2 \end{matrix} \xrightarrow[\text{Condensation}]{} \begin{matrix} CH\cdot C_6H_4\cdot NO \\ \| \\ CH\cdot C_6H_4\cdot NO_2 \end{matrix} \xrightarrow[\text{Oxidation}]{} \begin{matrix} CH\cdot C_6H_4\cdot NO_2 \\ \| \\ CH\cdot C_6H_4\cdot NO_2 \end{matrix}$$

On the other hand, 2:4-dinitrotoluene, like other derivatives of *p*-nitrotoluene with a strongly electro-negative ortho-substituent (CN, SO_3Ph, &c.), is far more reactive, giving an excessively unstable blue intermediate product, which is oxidised to tetranitrostilbene without the formation of any dibenzyl compound. The conclusion is drawn that the red intermediate products are nitronitrosodibenzyl derivatives, whilst the blue intermediate compounds are dinitrosostilbene derivatives, both classes of nitroso-compounds existing in an alkaline solution in the form of quinonoid alkali salts.

4:4′-*Dinitro*-2:2′-*dimethylstilbene*, obtained from *p*-nitro-*o*-xylene, forms yellow needles, which melt at 288—290°. 4:4′-*Dinitro*-2:2′-*dimethoxystilbene*, prepared from *p*-nitro-*o*-cresol methyl ether, crystallises in orange needles, melting at 268—269°. 4:4′-*Dinitrostilbene*-2:2′-*dicarboxylic acid*, obtained from nitro-*o*-toluic acid, crystallises from cresol in pale yellow crystals, which melt and decompose at 288—291°. 2:4:2′:4′-Tetranitrostilbene is formed by the action of cold alcoholic potash and iodine on 2:4-dinitrotoluene. 2:4:2′:4′-Tetra-aminostilbene forms pale yellow leaflets, which melt at 183—186° (Echales, *Ber.*, 1904, **37**, 3599, gives 191° or below).

198. "The solubility of lime in water."

By Gerald Tattersall Moody and Lewis Thomas Leyson.

The widely divergent numbers giving the solubility of lime in water recorded by previous observers are to be ascribed to the use of impure lime and to faulty methods of determining the solubility. The observed difference in the solubility of lime obtained from different sources is not ascribable to any peculiarity of the lime itself, but is due to the presence of impurities which either affect the solubility of the lime or are capable of neutralising acids, thereby causing an error wherever the lime present in solution is estimated by titration with acid.

An apparatus specially devised for eliminating the errors in method made by previous observers has allowed figures showing the solubility of lime between 2° and 80° to be obtained, and it is found that the curve of solubility between 25° and 80° is practically a straight line.

Thursday, October 22nd, 1908, at 8.30 p.m., SIR WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

Messrs. H. R. Lyell and C. T. Rutter were formally admitted Fellows of the Society.

The PRESIDENT referred to the loss sustained by the Society through the death, on August 25th, of Professor A. H. Becquerel, who was elected an Honorary and Foreign Member in May, 1904; also of Sir Thomas Stevenson and Mr. Bennett H. Brough, who died on July 27th and October 3rd, respectively.

On the question of admitting women to the Fellowship of the Chemical Society, the PRESIDENT announced that 1,758 voting papers were received before the close of the ballot; of these there were, in favour of admission, 1,094, against admission, 642, neutral, 22. The matter is now receiving the earnest attention of the Council.

The PRESIDENT further stated that he was authorised by the Council to inform the meeting that in all proceedings relating to the admission of women as Fellows, the Honorary Secretaries have throughout acted under the direction of the Council.

Certificates were read for the first time in favour of Messrs.:

Noel Charles Akers, 26, King's Avenue, Muswell Hill, N.
Maurice Barrett, Holly Bush, Headingley, Leeds.
Robert Bickerstaffe, Chilterns, Wooburn Green, Bucks.
William Sudderick Brakes, 137, Steade Road, Sheffield.
Leonard Clement, B.A., Beamsley, Fairhaven, near Lytham.
Robert Charles Cowley, College of Pharmacy and Chemistry, Brisbane.
Hugh Cecil Duckworth, 66, Victoria Street, S.W.
Horace Barratt Dunnicliff, B.A., B.Sc., 39, Herne Hill, S.E.
Reginald Freeman Easton, 38, Edith Road, W. Kensington.
Henry Fairburn, Northallerton.
Arthur Frank Girvan, B.Sc., 8, Chatsworth Road, West Norwood, S.E.
John Henry Albert Hebron, B.Sc., 9, Buller Street, Derby.
Grove Johnson, 124, Savoy Court, Strand, W.C.
Patrick Anderson Keiller, B.Sc., Colombo, Ceylon.
Frank William Linch, 9, Gladstone Avenue, Manor Park, London, E.
Arthur Stanley Lindley, Prince Building, Medows Street, Bombay.
Edward Pigott Minett, M.D., M.R.C.S., L.R.C.P., Guy's Hospital, S.E.
Cyril Lawrence Norman, 36, Halesworth Road, Lewisham, S.E.
Alexander Robert Normand, M.A., B.Sc., Wilson College, Bombay.

Alexander Rennie, Johannesburg, Transvaal.
Ezra Lobb Rhead, Stonycroft, Polygon Avenue, Levenshulme.
Maurice Salamon Salamon, 64, Oxford Gardens, N. Kensington, W.
William Saunderson, B.Sc., The Armidale School, Armidale, N.S.W.
Ernest Sommerfeldt, Ph.D., The University, Tübingen.
Francis George Henry Tate, Kilmersdon, Homecroft Road, Sydenham, S.E.
Robert Dickie Watt, M.A., B.Sc., P.O. Box 434, Pretoria, Transvaal.
Arthur Weighell, Prince Building, Medows Street, Fort, Bombay.
Frederick Williams, B.A., Bute Villa, Aberdare, South Wales.
William George Winterson, B.Sc., 89, Salisbury Road, Barnet.
Allister MacLean Wright, P.O. Box 617, Christchurch, New Zealand.

Of the following papers, those marked * were read:

***199. "The relationship of colour and fluorescence to constitution. Part II. Rhodamines of mellitic acid." By Oswald Silberrad and Charles Smart Roy.**

Condensation products of mellitic acid with *m*-aminophenol and dimethyl-*m*-aminophenol were described.

The results confirm the conclusions arrived at in the previous paper by one of the authors (Silberrad, *Trans.*, 1906, **89**, 1788), in indicating that a quinonoid structure is not an essential integral part of intensely coloured and fluorescent compounds.

The work also appears to show that the lactone ring is much more stable in these compounds than in the less complex phthaleins already known. As in the case of resorcinol compounds (*loc. cit.*), the tetra-aminodixanthyl derivatives exist in two modifications, in which the xanthyl groups are in the meta- and para-positions with regard to one another respectively. The orientation of these groups was determined by the introduction of a third xanthyl group in the case of the meta-compounds.

As both these still contain carboxylic groups in the ortho-position with respect to one another, the formation of trixanthyl derivatives from the meta-compounds only affords an exceptionally good example of steric hindrance.

The following new compounds, together with their salts and derivatives, were described:

Monoxanthyl derivatives.—3 : 6-*Diamino*-9-*hydroxyxanthylbenzene*-2-*carboxylactone*-3 : 4 : 5 : 6-*tetracarboxylic acid. Tetramethyl*-3 : 6-*diamino*-9 *hydroxyxanthylbenzenepentacarboxylic acid* and its *pentaethyl* ester. *Tetraethyl*-3 : 6-*diamino*-9-*hydroxyxanthylbenzenepentacarboxylic acid.*

Dixanthyl derivatives.—Octamethyl-3 : 3′ : 6 : 6′-*tetra-amino*-9 : 9′-*dihydroxy*-m-*dixanthylbenzene*-2 : 4 : 5 : 6-*tetracarboxylic acid* and its *ethyl* and *benzyl* esters. *Octaethyl*-3 : 3′ : 6 : 6′-*tetra-amino*-9 : 9′-*dihydroxy*-p-*dixanthylbenzene*-2 : 3 : 5 : 6-*tetracarboxylic acid* and its *ethyl* ester. *Tetramethyl* 3 : 6-*diaminotetraethyl*-3′ : 6′-*diamino*-9 : 9′-*dihydroxy*-m-*dixanthylbenzene*-2 : 4 : 5 : 6-*tetracarboxylic acid. Octaethyl*-3 : 3′ : 6 : 6′-*tetra-amino*-9 : 9′-*dihydroxy*-p-*dixanthylbenzene* 2 : 3 : 5 : 6-*tetracarboxylic acid.*

Trixanthyl derivatives.—Hydrated dodecamethyl-3 : 3′ : 3″ : 6 : 6′ : 6″-*hexa-amino*-9 : 9′ : 9″-*trihydroxy*-s-*trixanthylbenzene*-2 : 4 : 6-*tricarboxy-lactone* and its *triethyl* ester.

Discussion.

Prof. Green expressed the opinion that, although the case was more complicated, the facts described by Dr. Silberrad were not greatly different from those which held for the simple rhodamines, and the evidence for or against a quinonoid constitution was of about the same character. The non-formation of a potassium salt was also true of the simple rhodamines, whilst the resistance to esterification might be attributed to steric hindrance, owing to the carboxylic groups being placed between xanthyl residues.

Dr. Silberrad, in reply, considered that the action of alkalis on the trixanthyl derivatives, and their insolubility even in concentrated potassium hydroxide, must be regarded as strong evidence in favour of the lactonic formula. The mono- and di-xanthyl compounds, which were shown to be inner salts, possessed the properties of strong tetra- and penta-basic acids respectively.

As to the observation that the rhodamines also formed potassium salts only with the utmost difficulty, it seemed to him that this should be regarded as evidence of their lactonic structure rather than as indicative that the trixanthyl derivatives of mellitic acid, which showed the same lactone-like property, possessed a quinonoid structure.

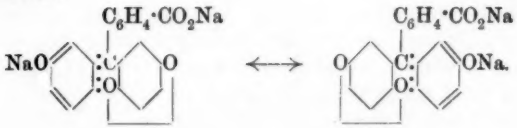
As to the possibility of steric hindrance being the explanation of the difficulty experienced in the esterification of the trixanthyl compounds, here again he thought that the evidence was in favour of the lactonic formula rather than the assumption of any such explanation, for if this were so, the formation of a tetraethyl ester from the meta-dixanthyl derivatives would offer more difficulty than the esterification of the para-compounds; experience showed, however, the converse to be the case, the meta-compound being the more readily esterified.

*200. **"Constitution of the salts of the phthaleins and the cause of colour in the triphenylmethane series." By Arthur George Green.**

Whilst strong evidence has been adduced in favour of the quinonoid structure of the coloured salts and ethers of the phthaleins, there still remain several facts which are not fully explained. One of these is the remarkable difference in colour between the quinonoid diethyl ethers and the alkali salts (orange in the first case and violet-red in the second), whilst another is the circumstance that the substitution of one only of the phenolic hydroxyl groups by methoxyl, in either phenolphthalein or in quinolphthalein, suffices entirely to prevent the formation of coloured salts with alkalis.

By an extension of von Baeyer's theory of oscillatory quinonoid bonds, employing the usual Fittig formula for quinonoid compounds instead of the Graebe formula used by von Baeyer, and by the assumption that the movement of the metallic or acid ion between the two salt-forming groups is the determining cause of the quinonoid oscillation, a satisfactory explanation can be given of the above and other facts, such as the effect of salt formation on colour intensity, the function of auxochromic groups, and the increase of basicity according to the "power law." An explanation is also afforded of the observation that the behaviour of dimethylanilinephthalein, the basic analogue of phenolphthalein, towards acids is analogous to that of the latter towards alkalis, these compounds giving under specific conditions a deep violet colour readily destroyed by an excess of the reagent.

In the quinolphthalein series, the possibility of a meta-quinonoid structure for the coloured alkali salts as suggested by R. Meyer was discussed in relation to the recent work of Green and King. The conclusion was drawn that the facts are best explained by the assumption of an ortho-quinonoid linking oscillating between the two benzene nuclei:



DISCUSSION.

Dr. SILBERRAD suggested that it would be a fuller and more complete explanation of the experimental evidence if colour were wholly attributed to some inner molecular oscillation, such as that so

well illustrated by the examples considered by Prof. Green, and not to the presence of a quinonoid group at all; thus the ethers of these compounds were almost colourless, yet they still contained the same quinonoid constitution, and differed from the parent compound only in that they could not exhibit inner molecular oscillation.

He agreed that the presence or absence of a quinone group exercised considerable influence on the colour of any compound, but so would any other considerable constitutional change.

Further, he thought that the wide application of the quinonoid configuration to coloured compounds by analogy was open to criticism. Prof. Green's observation, that the coloured salts of the rhodamines become colourless in the presence of an excess of acid, did not apply to their mellitic analogues, which yielded coloured solutions with any excess of acid.

Dr. MORGAN remarked that R. Meyer and Desamari's recent demonstration of the existence of tribromo-*m*-benzoquinone,

afforded important experimental evidence in favour of the view that certain phthaleins might have a meta-quinonoid structure.

In connexion with the theory that the colour of triphenylmethane dyes was associated with an oscillation of the quinonoid phase, it was noteworthy that diphenylnaphthylmethane dyes could be obtained from naphthastyril, a peri- or 1 : 8-derivative of naphthalene, because, owing to the configuration of the 1 : 8-naphthylene residue present in these colouring matters, it was difficult to see how this oscillation would take place.

***201. "The relation between absorption spectra and chemical constitution. Part X. Unsaturated acids of the benzene series." By Edward Charles Cyril Baly and Konrad Schaefer.**

The absorption spectra of cinnamylideneacetic, cinnamylidenemalonic, benzylidenemalonic, and cinnamic acids have been examined with a view to determining the influence of substitution of the acidic hydrogen atoms by metals and alkyl groups. In the case of cinnamylideneacetone, $C_6H_5\cdot CH{:}CH\cdot CH{:}CH\cdot \overset{\displaystyle O}{\overset{\|}{C}}\cdot CH_3$, a strongly marked absorption band is developed, owing to the isorropesis arising

from the conjugation of the carbonyl group with the two double linkings and the phenyl group. In cinnamylideneacetic acid, where the methyl group is replaced by hydroxyl, the absorption band is shifted towards the violet, owing to the fact that the free residual affinity of the carbonyl group is decreased by the juxtaposition of the hydroxyl group. This decrease of free residual affinity is most marked in the case of the readily ionised sodium salt, and least marked with the acid when the ionisation is restrained by the addition of hydrogen chloride. This effect has been observed in the four acids mentioned, and is especially marked in the case of cinnamylidenemalonic acid. The addition of alkali to this acid causes a shift of the absorption band from just inside the visible region to just beyond it, so that the free acid appears to be coloured yellow, and its sodium salt appears to be colourless. The results throw some light on the catalytic action of mineral acids on the esterification process.

***202. "Relation between chemical constitution and physiological action in certain substituted aminoalkyl esters." By Frank Lee Pyman.**

Several substituted aminoalkyl esters have been prepared with the object of producing a cocaine substitute; none of these, however, are suitable for the purpose, since such as possess anæsthetic properties are also toxic and irritant. These substances were prepared by benzoylating (in two cases, phthaloylating) the corresponding amino-alcohols, two of which, 1 : 4-*diethanolpiperazine* (m. p. 134—135°) and *β-hydroxy-β*·3 : 4-*methylenedioxyphenylethyldimethylamine*,* have not previously been described. The chemical, physical, and physiological properties of the following aminoalkyl esters and their salts have been examined: *dibenzoyloxymethyldiethylamine*, *dibenzoyloxytriethylamine*, *βγ-dibenzoyloxydimethylpropylamine*, *βγ-dibenzoyloxydiethylpropylamine*, *βγ-dibenzoyloxypiperidylpropane* (m. p. 64—65°), *piperidylethyl benzoate*, s-*di-β-benzoyloxy*-1 : 4-*diethylpiperazine* (m. p. 104—105°), *diethylaminoethyl phthalate*, *piperidylethyl phthalate*, *β-benzoyloxy-β*-3 : 4-*methylenedioxyphenylethyldimethylamine*.

203. "The passage of hydrogen through a palladium septum, and the pressure which it produces." By Demetrius Tsakalotos.

It was shown by Sir William Ramsay (*Phil. Mag.*, 1894, [v], **38**, 206) that hydrogen, when it passes through the walls of a palladium tube filled with a gas (N_2, CO, CO_2, CN) at atmospheric pressure, raises

* Where melting points are not given, the free base did not crystallise.

the pressure in the tube by nearly one atmosphere when the external pressure of the hydrogen is one atmosphere. There is always a small deficit in pressure, however, for the rise in pressure produced by the entry of the hydrogen never attains that of the atmosphere. The amount of this deficit depends on the nature of the gas originally in the tube.

The experiments to be recorded were made with the object of ascertaining whether, if the tube were initially filled with an indifferent gas, the final pressure would be the theoretical one. Argon was chosen for this purpose. The method employed differed little from that described by Ramsay. The tube was filled with pure dry argon at atmospheric pressure, and at a temperature of 280° (boiling point of bromonaphthalene); it was then exposed on its external surface to an atmosphere of hydrogen, carefully purified and dried. If p be the external pressure of the hydrogen, and p' the internal pressure, that is, the pressure due to the hydrogen after the gas had ceased to enter, the results of the experiments are as follow:

	I.	II.	III.	Theory.
p'/p	0·9281	0·9189	0·9242	1·000

The mean result is 0·9238.

This result does not appreciably differ from that previously obtained by Ramsay; the figures varied between 0·8984 and 0·9693.

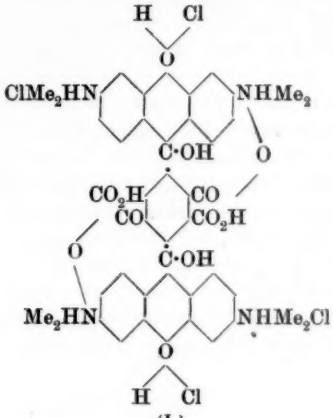
204. "Constitution of the phthaleins of mellitic and pyromellitic acids." By Oswald Silberrad.

In a previous paper, the author described (*Trans.*, 1906, **89**, 1789) condensation products of mellitic and pyromellitic acids with resorcinol to which were assigned carbinol formulæ, as being the most in accord with observed facts. Subsequently, quinonoid formulæ have been suggested (compare Green, *Proc.*, 1907, **23**, 12).

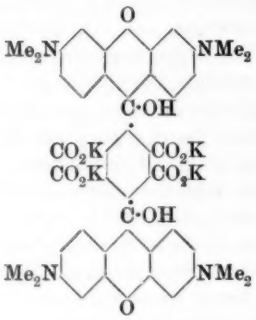
In considering the possibility of so formulating these compounds, it should not be lost sight of that the necessity for attributing quadrivalency to the pyrone oxygen atom is hardly in accord with the properties of the compounds in question; they show none of the basic properties generally attributed to this element when so linked; on the contrary, they form salts up to the full basicity of the acid groups present. Further, recent work by the author has shown that when present in analogous compounds a quadrivalent oxygen atom impresses a strongly basic influence on the specific properties of the compound.

Thus it has been shown that octamethyltetra-aminodixanthylbenzene-tetracarboxylic acid can behave as a base, forming a tetrahydro-

chloride (I), or as an acid, forming a tetrapotassium salt (II), according as the pyrone oxygen is quadrivalent or not.



(I.)



(II.)

205. "A new form of gas burette." By Arthur Edwin Hill.

A novel form of gas burette was described which consists of a series of ten bulbs, each with a capacity of 10 c.c., connected by short, narrow, graduated tubes. Fractional parts of 10 c.c. are measured in a narrow, side-tube, which has a capacity of 10 c.c. graduated into twentieths of a c.c.; this is connected to the main vessel by a capillary tube, and forms one arm of a U-shaped manometer, which indicates the pressure of the gas inside the burette. The apparatus is provided with a capillary tap at each end, and is connected by flexible rubber tube with a levelling reservoir.

206. "A molecular compound of trinitroacetylaminophenol and β-naphthol." By Raphael Meldola and James Gordon Hay.

The 2 : 3 : 5-trinitro-4-acetylaminophenol described by one of the authors in a former paper (*Trans.*, 1906, **89**, 1935) combines readily with β-naphthol when solutions containing equimolecular weights of the two compounds are mixed together and boiled for a few minutes. Acetic acid or alcohol can be used as a solvent. If the solution is not too dilute, the molecular compound separates out on cooling in dense, red prisms, melting with decomposition at 184—185° :

0·1196 gave 0·2216 CO_2 and 0·0392 H_2O. C = 50·33; H = 3·6.
0·0895 „ 9·9 c.c. N_2 (moist) at 14·5° and 755·8 mm. N = 12·89.
0·1245 „ 13·5 „ „ „ 10° „ 752·3 „ N = 12·85.
$C_8H_6O_8N_4,C_{10}H_8O$ requires C = 50·2; H = 3·23; N = 13·02 per cent.

That the compound is "molecular" is shown by its behaviour towards reagents. By alkali alone it is dissolved with an orange colour, which gradually disappears on standing, and, on acidifying, the solution yields only the products of decomposition of trinitroacetylaminophenol and β-naphthol. With alkali and dimethyl sulphate, the compound gives β-naphthyl methyl ether and the products of decomposition of the trinitroacetylaminophenol. By continued crystallisation from acetic acid, the compound is gradually resolved into its components.

The formation of this molecular compound is of interest as, so far, β-naphthol is the only phenol which has been found to enter into combination with the trinitro-compound. The latter, unlike picric acid and other polynitro-compounds, does not appear to form molecular compounds with hydrocarbons. This point is, however, still undergoing investigation, and the authors communicate this note as a preliminary statement of the results of their experiments.

207. "The products of reduction of azoxybenzene." (Preliminary note.) By Leslie Hamilton Berry.

The author is unable to confirm the statement of Schmidt and Schultz (*Ber.*, 1879, **12**, 484), that stannous chloride and hydrochloric acid reduce azoxybenzene to aniline, very little benzidine being formed.

He finds, on the contrary, that in no case is the yield of aniline more than 35 per cent., and the principal product is benzidine.

208. "The chlorination of para-nitroaniline." By Bernhard Flürscheim.

Hitherto no satisfactory method for introducing two atoms of chlorine into *p*-nitroaniline has been known. More especially by the action of chlorine gas much resinous matter was formed. The author finds, however, that a quantitative yield of pure dichloro-*p*-nitroaniline is obtained when *p*-nitroaniline is chlorinated in a mixture of acetic and mineral acids at a low temperature; this result is in accordance with theoretical deduction.

209. **"Syntheses with the aid of monochloromethyl ether. Part I. The action of monochloromethyl ether on the sodium derivatives of ethyl malonate and ethyl *iso*propylmalonate." By John Lionel Simonsen.**

Monochloromethyl ether and ethyl sodiomalonate readily condense with the formation of *ethyl β-methoxymethylmalonate*:

$$MeO{\cdot}CH_2Cl + CHNa(CO_2Et)_2 \longrightarrow MeO{\cdot}CH_2{\cdot}CH(CO_2Et)_2;$$

this is a colourless oil, which boils at 121—122°/15 mm. When hydrolysed with hydrochloric acid, it is converted into *cis-cyclo*butane-1 : 3-dicarboxylic acid. Other derivatives of ethyl β-methoxymethylmalonate have also been prepared.

When monochloromethyl ether and ethyl *iso*propylsodiomalonate are condensed, *ethyl β-methoxymethylisopropylmalonate* is formed:

$$MeO{\cdot}CH_2Cl + CNa(CHMe_2)(CO_2Et)_2 \longrightarrow MeO{\cdot}CH_2{\cdot}C(CHMe_2)(CO_2Et)_2.$$

This substance boils at 130—132°/20 mm., and, on hydrolysis, yields *β-methoxymethylisopropylmalonic acid*, which crystallises in plates, melting at 83—84°.

210. **"The effect of constitution on the rotatory power of optically active nitrogen compounds. Part III." By Reginald William Everatt and Humphrey Owen Jones.**

An account was given of the resolution of *p*-tolylbenzylmethylallylammonium hydrogen tartrate. The corresponding iodide has been prepared by Wedekind (1903), who found that the camphorsulphonate could not be resolved. This compound is of interest, since it contains two groups, benzyl and tolyl, which have the same mass. The salt of the lævorotatory base was isolated by crystallising about thirteen times from alcohol and ether.

The molecular rotatory power of the ion at 15° is −246°, that of the iodide in alcohol is −257°, and in chloroform is −267°.

The rotatory power of the ion is greater than that of the ion of the corresponding phenyl (167°) or *p*-bromophenyl compound (191°). This is not in agreement with the requirements of Guye's hypothesis as applied to the case of nitrogen, and shows that the constitution of a group may exert such a marked effect on the rotatory power of a compound as to veil completely the effect of mass.

211. **"Studies on the cobaltinitrites." By Mary Cunningham and Frederick Mollwo Perkin.**

On adding a solution of a salt of a primary amine to a strong solution of sodium cobaltinitrite, a yellow or orange precipitate is

produced, which is frequently crystalline. If the solution is not kept cold, the product is apt to decompose. Analysis shows that three molecules of the amine combine with the cobaltinitrite residue. Thus the compound obtained from methylamine has the formula

$$(CH_3 \cdot NH_3)_3Co(NO_2)_6.$$

The authors have prepared the methylamine, ethylamine, aniline, *m*- and *p*-bromoaniline, and the *p*-toluidine compounds, all of which have been analysed. It is found that, unless carefully dried as soon as prepared, the compounds are extremely unstable, and even then it is necessary to analyse them very soon after preparation. Diethylamine also forms a crystalline compound, $[(C_2H_5)_2NH_2]_3Co(NO_2)_6$, which is fairly stable. The methylaniline compound decomposes before it can be dried, and apparently a nitroso-compound is produced. From dimethylaniline, the *p*-nitroso-derivative is at once formed.

212. "The relation between viscosity and chemical constitution. Part II. The existence of racemic compounds in the liquid state." By Albert Ernest Dunstan and Ferdinand Bernard Thole.

The authors have applied the viscosimetric method to the above problem, and have determined the viscosities at 25° of the active and inactive forms of tartaric acid, malic acid, pinene, camphene, and limonene.

They find that in general the inactive form has the lower viscosity, and argue that this points to the existence as such of the racemic compound in the liquid state.

They have further examined the viscosity of solutions of sodium ammonium tartrate at different temperatures, and find that a change of curvature appears at 28·7°; hence a new method of determining transition points is to be added to those already in vogue.

213. "The formation of polyiodides in nitrobenzene solution. Part IV. The electrolytic dissociation of the polyiodides of the alkali metals and ammonium radicles." By Harry Medforth Dawson and Colin Gyrth Jackson.

The authors have investigated the electrolytic dissociation of the polyiodides in nitrobenzene solution by means of freezing-point and electrical conductivity measurements. The data obtained show that the polyiodides are ionised to a considerable extent.

In the case of the polyiodides of potassium, for which several series of freezing-point measurements were made, the depressions, calculated

from the chemical dissociation on the assumption that the higher polyiodides are ionised to the same extent as the tri-iodide, are in good agreement with the observed values. It is probable that the penta-, hepta-, and ennea-iodide of each alkali metal and ammonium base are equally ionised, although the degree of ionisation appears to vary with the nature of the cation. On the other hand, evidence has been obtained that, in some cases, the tri-iodides are not ionised to the same extent as the higher polyiodides.

As the result of comparative measurements of the conductivity of solutions of the iodides and tri-iodides, it is found that the tri-iodides are electrolytically dissociated to a much greater extent than the iodides. In the case of tetrapropylammonium iodide, for which, on account of its solubility in nitrobenzene, a comparison by the freezing-point method has been possible, the conclusions drawn from the conductivity data are completely confirmed.

The mobilities of the polyiodide ions have been deduced by combining the results of transport measurements with the freezing-point and conductivity data.

Finally, determinations of the molecular solution-volume of iodine and the polyiodides have been made. The results show that the volume of combined iodine differs from that of iodine in the free condition.

214. "The direct action of radium on copper and gold." By Edgar Philip Perman.

The direct action of the radiations from a radium salt on a pure copper salt has been investigated; the salts were placed in small capsules facing one another in a wide tube, which was exhausted and sealed.

In the case of gold, the two salts were left in solution together, and in another experiment, gold and radium barium sulphate were precipitated together, thoroughly washed, and allowed to stand.

After four months, no trace of lithium could be detected by spectroscopic examination, and the conclusion is drawn that if any copper or gold is converted into lithium, it cannot be more than the one hundred-millionth part of the weight of the radium salt per day in the case of copper, and the one two-hundred-millionth part in the case of gold, under the conditions of the respective experiments.

215. "The atomic volumes of phosphorus. Part II. Phosphorus and bromine." By Edmund Brydges Rudhall Prideaux.

The specific volumes of liquid phosphorus pentabromide and the pressures of its saturated vapour at various temperatures have been

measured. From the values of the vapour pressures from 20° to 100°, and of the coefficients of expansion and molecular volumes from 85° to 100° and 100° to 165°, the true boiling point is placed at 106°, and the molecular volume at this temperature is 157·3. A review of the molecular volumes of the chlorides, bromides, phosphoryl chloride, and phosphoryl dichlorobromide shows that the atomic volumes of tervalent are greater than those of quinquevalent phosphorus.

216. "Isomeric chromous chlorides." By Elizabeth Mary Rich.

The author has devised a rapid and convenient method of preparing pure chromous chloride, which is thus rendered practically available for use in all kinds of gas analysis. Two isomeric series of hydrates and their solutions have been studied. The green isomeride has the formula $CrCl_2,4H_2O$, identical with the blue salt. Its green solution contains the ions $CrCl^{\cdot}$ and Cl'.

217. "The relative atomic weights of hydrogen and chlorine." By Robert Whytlaw Gray and Frank Playfair Burt.

The ratio H : Cl has been measured by a method which is different from that employed by Dixon and Edgar (*Phil. Trans.*, 1905, **205**, 169) or by Noyes and Weber (*J. Amer. Chem. Soc.*, 1908, **30**, 13). The investigation was carried out with hydrogen chloride obtained from several sources, and purified by fractional distillation. (1) The density of the gas was determined, the gas being condensed on charcoal and weighed. The mean of twenty experiments gave for the weight of a normal litre of gas the value $1{\cdot}63900 \pm 0{\cdot}00004$ grams, or making a small correction for the amount of gas condensed on the surface of the walls of the density bulb and absorbed by the tap grease, 1·63885 grams. (2) The gas was analysed volumetrically by passage over heated aluminium. By this means the volume of hydrogen contained in exactly two volumes of hydrogen chloride measured at 0° and 760 mm. was determined, and this gave the exact ratio of the volumes of hydrogen and hydrogen chloride which under standard conditions contain the same number of molecules.

Eight measurements with gas from different sources gave for the volume ratio $\frac{H_2}{HCl}$ the mean value $1{\cdot}00790 \pm 0{\cdot}00002$.

From these two results, the molecular weight of hydrogen chloride may be directly calculated as follows:

If D_{HCl} represents the measured weight of a litre of hydrogen chloride at 0° and 760 mm., lat. 45°, and D_{H_2} represents the known

weight of a litre of hydrogen at 0° and 760 mm., lat. 45°, and if $\frac{V_{H_2}}{V_{HCl}}$ expresses the ratio of the volumes of hydrogen and hydrogen chloride, which at 0° and 760 mm. contain the same number of molecules: then the molecular weight of hydrogen chloride is given by the expression $\left(\frac{D_{HCl}}{D_{H_2}} \times \frac{V_{HCl}}{V_{H_2}}\right) \times 2$.

On the basis of Morley's values for the normal density of hydrogen, namely, 0·089873 gram per litre, and for the atomic weight of hydrogen, namely, 1·00762, the molecular weight of hydrogen chloride is $\left(\frac{1·63885}{0·089873} \times \frac{2}{1·00790}\right) 1·00762 = 36·461$, and the atomic weight of chlorine = 35·453. This agrees almost exactly with the results of Noyes and Weber, namely, Cl = 35·452, but is $\frac{1}{3500}$ part lower than Dixon and Edgar's number, namely, 35·462.

218. "The interaction of hydrogen dioxide and sulphides." By Maud Gazdar and Samuel Smiles.

The usual method of preparing sulphoxides from sulphides by means of concentrated nitric acid is useless when applied to sensitive compounds, such as di-*p*-aminophenyl sulphide or thiodiglycollic acid. Hydrogen dioxide in acetone or aqueous solution reacts at the ordinary temperature with the sulphides, giving almost quantitative yields of the corresponding sulphoxide. The reaction can be applied to sulphides of very varied character, for, besides amyl, benzyl, and phenetyl sulphoxides, the hitherto unknown *di-p-aminophenyl sulphoxide* and *thionyldiglycollic acid* were obtained. Diphenylene disulphide and tetranitrodiphenyl disulphide are not attacked by the reagent under ordinary conditions.

219. "The influence of solvents on the rotation of optically active compounds. Part XIII. Ethyl tartrate in aromatic nitro-derivatives. Influence of temperature change on rotation in solution." By Thomas Stewart Patterson.

The influence of the aromatic nitro-derivatives as solvents on the rotation of ethyl tartrate was described. The effect of temperature-change on the rotation of these and other solutions was also discussed.

220. "The isomeric menthols." (Preliminary note.) By Robert Howson Pickard and William Oswald Littlebury.

According to theory there should be eight optically active forms of 1-methyl-4-*iso*propyl*cyclo*hexan-3-ol corresponding in pairs with four racemic compounds. Of these menthols, one, the ordinary *l*-menthol, occurs in nature, whilst the existence of others has been indicated by the researches of Beckmann, Kondakoff, and Brunel. It is now found that these compounds can be separated by the fractional crystallisation of suitable esters, such as the hydrogen phthalates, hydrogen succinates, etc.

By the reduction of thymol with hydrogen in the presence of reduced nickel, Brunel (*Compt. rend.*, 1905, **140**, 252) obtained a low-melting thymomenthol, which he considered was transformed into an isomeride by conversion into an ester and subsequent hydrolysis. The authors have been able to show that this "*a*" thymomenthol of Brunel contains three (or perhaps all four) of the racemic compounds mentioned above. Up to the present, two of these have been fully characterised and resolved into their optically active components by fractional crystallisation of various alkaloidal salts of some of their acid esters (compare Pickard and Littlebury, *Trans.*, 1907, **91**, 1974).

The first of these racemic menthols melts at 25°, and forms a *hydrogen succinate*, m. p. 86°, and also a *hydrogen phthalate*, m. p. 131°, the latter of which by fractional crystallisation of either its cinchonine or brucine salt yields a lævorotatory isomeride. When hydrolysed, this lævo-ester yields a menthol identical in melting point and rotation with the natural menthol.

The second of the racemates melts at 48—50°, and forms a *hydrogen phthalate*, m. p. 175—177°, which is readily resolved into its active components by crystallisation of the brucine salt.

ADDITIONS TO THE LIBRARY.

I. *The following books have been presented to the Library by Mr. A. W. Soward:*

Clarke, *John.* A demonstration of some of the principal sections of Sir Isaac Newton's Principles of Natural Philosophy. In which his peculiar method of treating that useful subject is explained, and applied to some of the chief phænomena of the system of the world. pp. xvi + 313 + vii. London 1730.

Euler, *Leonhard.* Letters of Euler to a German Princess, on differ-

ent subjects in physics and philosophy. Translated from the French by *Henry* **Hunter**. 2 vols. pp. lxiii + 515, viii + 520 + xxviii. ill. London 1795.

Macbride, *David*. Experimental essays on medical and philosophical subjects: Particularly, I. On the fermentation of alimentary mixtures, and the digestion of the food. II. On the nature and properties of fixed air. III. On the respective powers, and manner of acting, of the different kinds of antiseptics. IV. On the scurvy . . . V. On the dissolvent power of quick-lime; and a further investigation of the properties of fixed air. 2nd edition. pp. xiv + 296. ill. London 1767.

Martin, *Benjamin*. An essay on electricity. pp. 40. London 1746.

——— A panegyrick on the Newtonian philosophy. 2nd edition. pp. 62. London 1754.

——— Microscopium Polydynamicum: or, a new construction of a microscope. pp. 10. ill. London 1771.

——— Thermometrum Magnum: or, grand standard thermometer. Expressing all degrees of heat and cold, from that with which mercury boils, to that which congeals it into solid metal. pp. vi + 10. London 1772.

——— A description of the nature, construction, and use of the Torricellian, or simple barometer. pp. 24. ill. London 1778.

Martine, *George*. Essays on the construction and graduation of thermometers, and on the heating and cooling of bodies. A new edition, with notes and considerable additions, especially the tables of the different scales of heat, exhibited by Dr. Black, in his annual course of chemistry. pp. vi + 186. ill. Edinburgh 1792.

Muspratt, *James Sheridan*. Chemistry, theoretical, practical, and analytical, as applied and relating to the arts and manufactures. Division I. pp. 288 [plates missing]. Glasgow [*no date*].

Nollet, *Jean Antoine*. Leçons de physique expérimentale. 6 vols. [Vols I & II, 3rd edition; Vols. III & V, 2nd edition; Vols. IV & VI, 1st edition.] pp. lviii + 379, 489, 512, 535, vi + 592, 527. ill. Paris 1748—1764.

Vauquelin [*Louis Nicolas*]. Manuel complet de l'essayeur, suivi de l'instruction de Gay-Lussac, sur l'essai des matières d'argent par la voie humide, et des dispositions du laboratoire de la monnaie de Paris; par D'Arcet. Nouvelle edition . . . par *A. D.* **Vergnaud**. pp. 248. ill. Paris 1836.

Violette, *Henry*. Nouvelles manipulations chimiques simplifiées, . . . contenant la description d'appareils simples et nouveaux, suivi d'un cours de chimie pratique à l'aide des instruments. 3rd edition. pp. iv + 476. ill. Paris 1860.

II. *By Purchase.*

Congrès international de chimie appliquée (II). Comptes rendus. 5 vols. pp. 773, 540, 499, 659, 260. ill. Paris 1897. (*Recd.* 10/6/08.)

Post, *Julius*. Chemisch-technische Analyse. Edited by *Bernhard* **Neumann**. Vol. II, part 3. pp. 660 to 1048. ill. Braunschweig 1908. (*Recd.* 11/8/08.)

Priestley, *Joseph*. Experiments and observations on different kinds of air. Vol. I. pp. 324. [Wanting pp. i—xxviii.] London 1774. (*Recd.* 3/6/08.)

Procter, *Henry Richardson*. Leather industries laboratory book of analytical and experimental methods. 2nd edition. pp. xx + 460. ill. London 1908. (*Recd.* 8/8/08.)

Zopf, *W.* Die Flechtenstoffe in chemischer, botanischer, pharmakologischer und technischer Beziehung. pp. xi + 450. ill. Jena 1907. (*Recd.* 27/5/08.)

III. *Pamphlets.*

Hooper, *David*. Fat of the Himalayan Bear. (From the *J. and Proc., Asiatic Soc. of Bengal.* **4**, 1908.)

——— Oil of *Lawsonia alba*, Lamk. (From the *J. and Proc., Asiatic Soc. of Bengal.* **4**, 1908.)

Lucas, *A.* The chemistry of the river Nile. pp. 78. Cairo 1908.

——— A preliminary note on some preservative materials used by the Ancient Egyptians in connection with embalming. (From the *Cairo Scientific Journal.* **2**, 1908.)

Pittman, *E. F.* Problems of the artesian water supply of Australia, with special reference to Professor Gregory's theory. [*Clarke Memorial Lecture delivered before the Royal Society of New South Wales*, 31st October, 1907.] pp. 30. Sydney 1908.

Power, *Frederick B.*, and **Tutin**, *Frank*. Chemical examination of Grindelia, Part II. (From the *Proc. Amer. Pharm. Assoc.* **55**, 1907.)

Reade, *T. Mellard*, and **Holland**, *Philip*. Analyses of Longmyndian Rocks. (From the *Proc. Liverpool Geol. Soc.* 1907—1908.)

York Health and Housing Reform Association. The milk supply of York. pp. 19. York 1908.

RESEARCH FUND.

A Meeting of the Research Fund Committee will be held in December next. Applications for Grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on, or before, Monday, December 7th, 1908.

All persons who received Grants in December, 1907, or in December of any previous year, whose accounts have not been declared closed by the Council, are reminded that reports must be in the hands of the Hon. Secretaries not later than Tuesday, December 1st.

The Council wish to draw special attention to the fact that the income arising from the donation of the Worshipful Company of Goldsmiths is to be more or less especially devoted to the encouragement of research in Inorganic and Metallurgical Chemistry. Furthermore, that the income due to the sum accruing from the Perkin Memorial Fund is to be applied to investigations relating to problems connected with the Coal-tar and Allied Industries.

At the next Ordinary Meeting, on **Thursday**, November **5**th, 1908, at **8.30** p.m., the following papers will be communicated:

"The direct union of carbon and hydrogen." By W. A. Bone and H. F. Coward.

"The relation between absorption spectra and chemical constitution. Part XI. Some aromatic hydrocarbons." By E. C. C. Baly and W. B. Tuck.

"Organic derivatives of silicon. Part VII. Synthesis of *dl*-sulphobenzylethyl*iso*butylsilicyl oxide." By B. D. W. Luff and F. S. Kipping.

"Chlorine derivatives of pyridine. Part IX. Preparation and orientation of the dichloropyridine, m. p. 66—70°." By W. J. Sell.

"Chlorine derivatives of pyridine. Part X. Orientation of the trichloropyridine, m. p. 49—50°." By W. J. Sell.

"Chlorination of methyl derivatives of pyridine. 2-Methylpyridine. Part II." By W. J. Sell.

"The triazo-group. Part V. Resolution of α-triazopropionic acid." By M. O. Forster and H. E. Fierz.

"The triazo-group. Part VI. Triazoethyl alcohol and triazoacetaldehyde." By M. O. Forster and H. E. Fierz.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 24 No. 346

Thursday, November 5th, 1908, at 8.30 p.m., SIR WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

Mr. G. J. Fowler was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs.:

Thomas James Baker, D.Sc., Trebarwith, Chester Road, Erdington, Birmingham.
Charles Everitt, M.A., 67, Boston Avenue, Southend-on-Sea.
Henry Hamilton Green, 36, Princes Square, Regent Park, Glasgow.
Edward Hinks, B.Sc., 23, Tavistock Road, Croydon.
Joseph Kenyon, B.Sc., 6, Cheltenham Street, Blackburn.
Gregor MacGregor, M.A., B.Sc., Giffen Park, Dysart, Fife.
William Herbert Miles, 3, Liversidge Road, Higher Tranmere, Birkenhead.
Charles James Millar, c/o Messrs. Turner, Morrison & Co., Calcutta.
George Edward Pearson, c/o Messrs. Burroughs, Wellcome & Co., Snow Hill Buildings, E.C.
Frank Moreton Thomas, 290, Rotton Park Road, Edgbaston, Birmingham.
Sidney Gilbert Walton, "Kensington," Northwood Road, Northwood, Lane Cove River, N.S.W.
William Ord Wootton, B.Sc., 159, Maidstone Road, Rochester.
Frederick Palliser Worley, M.A., M.Sc., Mansfield House, Clifton Gardens, Maida Hill, W.

Of the following papers, those marked * were read :

***221. "The direct union of carbon and hydrogen. Synthesis of methane." By William Arthur Bone and Hubert Frank Coward.**

The recent work of Berthelot, Pring and Hutton, and Mayer and Altmayer on this subject was critically reviewed. The results of new experiments were described which demonstrate the formation of large quantities of methane when less than 0·1 gram of sugar-charcoal (highly purified by prolonged ignition in dry chlorine, first of all at 700° and then at 1100°) is heated in a stream of pure dry hydrogen to between 1100° and 1200° in an apparatus similar to that used by Bone and Jerdan in 1897.

In two separate experiments, the yields of methane (namely, 137·0 c.c. and 125·5 c.c. at 0° and 760 mm. from 0·0995 and 0·092 gram of carbon respectively) were as much as 73 per cent. of those theoretically obtainable, the remainder of the methane being lost by unavoidable oxidation or decomposition in contact with the intensely hot walls of the porcelain tube in which the carbon was heated. In one group of four experiments, the formation of altogether 422 c.c. of methane from 0·306 gram of carbon was demonstrated. The authors therefore consider that the synthesis of methane from its elements, as originally carried out by Bone and Jerdan in 1897 and 1901, is fully confirmed.

Incidentally, the results of analyses of the sample of highly purified carbon originally used by Bone and Jerdan were given, showing that the hydrogen in it did not exceed 0·06 per cent., of which at least part would be occluded.

Discussion.

Dr. Lowry, as evidence of the unreliability of thermodynamic calculations of high temperature equilibria, referred to the case of nickel oxide, where the pressure of oxygen at 1127° had been calculated by Stahl (*Metallurgie*, 1907, **4**, 682) as 0·000000033 mm., the values actually observed (Foote and Smith, *J. Amer. Chem. Soc.*, 1908, **30**, 1349) being 5·5 mm. at 1100° and 13·0 mm. at 1200°. The value calculated for 227° was $1{\cdot}859 \times 10^{-45}$, or roughly $0{\cdot}5 \times 10^{-21}$ molecule per 22·4 litres, and in the case of zinc oxide, $1{\cdot}333 \times 10^{-67}$ or $0{\cdot}3 \times 10^{-43}$ molecule, figures which, in spite of the formal exactness, were of such ultra-electronic minuteness as to have no significance whatever.

Dr. Feilmann asked whether Prof. Bone could supply information as to the black substance formed by the methane on the walls of the porcelain tube in which the reaction took place, and suggested that it

might contain carbon, due to decomposition of the methane formed; such decomposition might be promoted both by the walls of the tube being presumably rather hotter than the body of the gas, and also by the special action which was well known to be peculiar to solid surfaces in similar circumstances. It was difficult to believe that the coloration could be due to the formation of silicon in the porcelain, and it presumably contained no lead.

Prof. BONE, in reply, wished it to be understood that he did not attack Nernst's thermodynamical arguments as being, from the abstract point of view, unsound—this not being the point raised in the paper—but merely contended that for calculating high temperature equilibria they were at present useless, owing to defective knowledge of the measure of the thermal factors involved. There was nowadays a tendency, in certain quarters, to overestimate the value of mathematical deductions in relation to chemical phenomena, and it was necessary to protest against the practice of setting aside the results of carefully conducted experiments on merely mathematical grounds.

In answer to Dr. FEILMANN, he was afraid he could give no definite information as to what particular constituent of the porcelain or the glaze of the inner tube had been reduced by the methane; presumably it might be the silica, and certainly the appearance of the tube suggested this. With regard to the mechanism of the process, it might be either a direct reduction by methane itself, or a secondary effect due to carbon liberated by a primary decomposition of methane in contact with the hot surface.

***222. "The relation between absorption spectra and chemical constitution. Part XI. Some aromatic hydrocarbons." By Edward Charles Cyril Baly and William Bradshaw Tuck.**

The authors have examined the absorption spectra of the following hydrocarbons: naphthalene, acenaphthene, acenaphthylene, fluorene, chrysene, anthracene, phenanthrene, diphenyl, and dibenzyl. Certain minor differences from Hartley's observations of naphthalene, anthracene, and phenanthrene (*Trans.*, 1881, **39**, 153; 1885, **47**, 685) have been noted. In some cases the absorption of the hydrocarbons shows considerable similarity among themselves, from which it has been found possible to gain some insight into the dynamic condition of these substances.

***223. "Organic derivatives of silicon. Part VII. The synthesis of *dl*-sulphobenzylethyl*iso*butylsilicyl oxide." By Bernard Dunstan Wilkinson Luff and Frederic Stanley Kipping.**

The only optically active silicon compounds which have hitherto been described, namely, the *d*- and *l*-forms of sulphobenzylethylpropylsilicyl oxide,

$$SO_3H\cdot C_6H_4\cdot CH_2\cdot SiEtPr\cdot O\cdot SiEtPr\cdot CH_2\cdot C_6H_4\cdot SO_3H,$$

have very low specific rotations, and in many cases when they are combined with a given optically active base their enantiomorphous relationship is not very clearly indicated.

Although there can be no doubt that the molecules of these acids are asymmetric, it seemed desirable to prepare, if possible, some other compound of the same type. With this object, the authors have synthesised *benzylethyl*isobutylsilicyl chloride, $SiEt(C_7H_7)(C_4H_9)Cl$, b. p. 198—202° (100 mm.); *benzylethyl*isobutylsilicol, $SiEt(C_7H_7)(C_4H_9)\cdot OH$, b. p. 162—164° (25 mm.), and *benzylethyl*isobutylsilicyl oxide,

$$[SiEt(C_7H_7)(C_4H_9)]_2O,$$

b. p. 250—252° (20 mm.). Each of these three substances was then sulphonated with the aid of chlorosulphonic acid, and also in the case of the silicol and the oxide with concentrated sulphuric acid. The product in all cases was a mixture from which the same *dl*-acid, namely, dl-*sulphobenzylethyl*isobutylsilicyl oxide, was isolated in the form of its l-*menthylamine* salt; this compound,

$$[SiEt(C_4H_9)\cdot CH_2\cdot C_6H_4\cdot SO_3H]_2O,2C_{10}H_{21}N,4H_2O,$$

melts at 240—245°, and its specific rotation is $[\alpha]_D^n$ −14·7° in methylalcoholic solution; it is not resolved by fractional crystallisation.

From the *l*-menthylamine derivative, the *sodium* salt of the pure *dl*-acid was obtained, and from the latter the d-*bornylamine*, *cinchonidine*, and *cinchonidine hydrogen* salts were prepared.

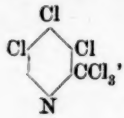
Experiments on the resolution of this *dl*-acid will be described at an early date.

***224. "The relation between viscosity and chemical constitution. Part III. The enol-ketonic tautomerism." By Albert Ernest Dunstan and James Arthur Stubbs.**

The authors have investigated the viscosity of ethyl acetoacetate, ethyl ethylacetoacetate, and ethyl diethylacetoacetate, alone and in various solvents. They have also studied the effects of piperidine and sodium ethoxide on ethyl acetoacetate. In confirmation of the work of Brühl, Perkin, Drude, Schaum, Knorr, and Lowry on these and similar compounds, they conclude that ethyl acetoacetate is mainly existent in the ketonic condition.

225. "The chlorination of methyl derivatives of pyridine. Part II. 2-Methylpyridine." By William James Sell.

When α-picoline hydrochloride saturated with hydrogen chloride is chlorinated at 105—110° until no further action is apparent, an oily mixture of chlorinated derivatives is obtained, which, on the removal of the excess of chlorine and hydrogen chloride by a current of dry air, partly solidifies. The solid compound thus obtained was shown (Part I, *Trans.*, 1905, **87**, 799) to have the constitutional formula :



and the author has now examined the liquid part of the products. The chief constituent of this oily liquid is *pentachloropicoline*,

$$C_5H_2Cl_2N\cdot CCl_3.$$

This compound readily yields 3 : 5-*dichloropicolinic acid*, which crystallises from water in needles melting at 153—154°. The *methyl* ester and the *amide* have been prepared. On heating, the acid is converted into 3 : 5-*dichloropyridine*, m. p. 66—67°.

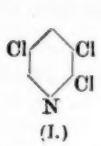
226. "The chlorine derivatives of pyridine. Part IX. Preparation and orientation of 3:5-dichloropyridine." By William James Sell.

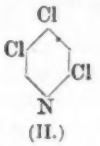
The well-marked basic characters of this substance, together with its great stability, suggested that the chlorine atoms in this compound occupy the 3 : 5 position. This conclusion is strengthened by the analogy in general properties and stability under similar conditions to the dibromopyridine, m. p. 110—111°, in which the bromine atoms are known to occupy the positions 3 : 5. The orientation was carried out by converting specimens of the 3 : 5-dibromopyridine and the dichloropyridine in question into diethoxypyridine, and showing that the diethoxypyridines from the two sources yield identical compounds with bromine and with chlorine.

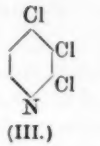
227. "The chlorine derivatives of pyridine. Part X. Orientation of 2 : 3 : 5-trichloropyridine." By William James Sell.

Excluding the trichloropyridines of known constitution, and having regard to the feeble, but distinct, basic properties of the compound in

question, there seemed every probability that its constitution should be represented by one of the following formulæ:


(I.)


(II.)


(III.)

of which (I) was regarded as sufficiently probable to warrant the attempt to determine its constitution on the following lines.

Such a compound ought to be attacked by ammonia, giving 3 : 5-dichloro-2-aminopyridine. This was carried out, and a substance melting at 84—85° was isolated. Further, 3 : 5-dichloropicolinamide (this vol., p. 225) was converted by the Hofmann reaction into 3 : 5-dichloro-2-aminopyridine.

The compound thus prepared melted at 84—85°, and the melting point was unaffected by admixture with the specimen obtained by the action of ammonia on the trichloropyridine in question. Moreover, Königs and Geigy have described (*Ber.*, 1884, **17**, 589, 1833) a dichloroethoxypyridine obtained from this trichloropyridine by the action of sodium ethoxide. This substance was converted into the dichlorohydroxypyridine, m. p. 178°, by heating with hydrochloric acid.

Finally, 3 : 5-dichloro-2-aminopyridine was converted by a modification of the Bouveault reaction into the same dichlorohydroxypyridine, m. p. 178—179°, as was obtained from the trichloropyridine in question.

228. "The triazo-group. Part V. Resolution of α-triazopropionic acid." By Martin Onslow Forster and Hans Eduard Fierz.

l-α-*Triazopropionic acid*, $CH_3 \cdot CHN_3 \cdot CO_2H$, has the specific gravity 1·2293 compared with water at 21°, and $[\alpha]_D$ −2·27°; a 16 per cent. solution in ether has $[\alpha]_D$ −28·9°, and a 21 per cent. solution in water, $[\alpha]_D$ +4·8°. The *brucine* salt, $C_{26}H_{31}O_6N_5$, has not a definite melting point, but evolves gas at about 150°; the aqueous solution displays mutarotation, the permanent value being $[\alpha]_D$ −26·4° in a concentration of 4 per cent. The *ethyl* ester, $C_5H_9O_2N_3$, boils at 49° under 5 mm. pressure, has specific gravity 1·063 compared with water at 22°, and $[\alpha]_D$ −18·2°; the *amide*, $C_3H_6ON_4$, melts at 85° and is dextrorotatory, having $[\alpha]_D$ 49·1° in water. When *l*-α-triazopropionic acid is reduced with aluminium amalgam, *d*-alanine is formed.

229. "The triazo-group. Part VI. Triazoethyl alcohol and triazoacetaldehyde." By Martin Onslow Forster and Hans Eduard Fierz.

Triazoethyl alcohol (2-*triazoethanol*-1), $N_3 \cdot CH_2 \cdot CH_2 \cdot OH$, prepared from ethylene chlorohydrin and sodium azide, is a colourless, sweet-tasting, odourless liquid, having specific gravity 1·149 compared with water at 24°, and boiling at 60° under 8 mm. pressure; treatment with stannous chloride eliminates nitrogen and produces aminoethyl alcohol. *Triazoethyl acetate*, $CH_3 \cdot CO_2 \cdot C_2H_4N_3$, has specific gravity 1·126 compared with water at 24°, and boils at 74° under 20 mm. pressure; the odour is much more pronounced than that of ethyl triazoacetate, resembling that of ethyl acetate in character and intensity.

Triazoethyl p-*nitrobenzoate*, $NO_2 \cdot C_6H_4 \cdot CO_2 \cdot C_2H_4N_3$, melts at 82°, and, on reduction with tin and hydrochloric acid, yields p-*aminobenzoyloxyethylamine*, $NH_2 \cdot C_6H_4 \cdot CO_2 \cdot C_2H_4 \cdot NH_2$, which melts at 78° when crystallised with $1H_2O$, the anhydrous base melting at 122·5°; the *picrate* and *dibenzoyl* derivative melt at 172—175° and 212° respectively.

Triazoacetaldehyde, $N_3 \cdot CH_2 \cdot CH{:}O$, obtained from chloroacetaldehyde hydrate and sodium azide, is an oil, which has not been purified on account of the readiness with which it undergoes change on heating or when treated with various agents; its behaviour towards alkalis resembles that of the triazo-ketones.

230. "Contribution to the chemistry of the cholesterol group. Part II. Some oxidation products of sitosterol." By Robert Howson Pickard and Joseph Yates.

The behaviour on oxidation of the vegetable cholesterol, sitosterol, has been studied. This alcohol, which is obtained from the fat contained in wheat, yields oxidation products which are analogous to those given by cholesterol itself.

Using a nomenclature similar to that of Windaus (*Arch. Pharm.*, 1908, [ii], **246**, 117) for cholesteryl derivatives, the following are the products obtained:—by the action of hydrogen peroxide on sitosterol, *dehydrositostanetriol*, $C_{27}H_{46}O_3$, m. p. 252°, and its *diacetate*, m. p. 138—139°; by the action of chromium trioxide on the triol, *dehydrositostanedionol*, $C_{27}H_{42}O_3$, m. p. 256°; by the action of dehydrating agents on the dionol, *dehydrositostenedione*, $C_{27}H_{40}O_2$, m. p. 166°, and its *monophenylhydrazone*, m. p. 247°; by the action of zinc dust on the unsaturated dione, *dehydrositostanedione*, $C_{27}H_{42}O_2$, m. p. 196°, and its

dioxime, m. p. 187°; by the oxidation of the saturated dione with chromium trioxide, a *ketodicarboxylic acid*, $C_{27}H_{42}O_5$, m. p. 236°, and its *dimethyl* ester, m. p. 107°, and also the *oxime* of the ester, m. p. about 90°.

231. "Experiments on the synthesis of the terpenes. Part I (cont.). Resolution of *dl*-1-methyl-Δ^1-*cyclo*hexene-4-carboxylic acid and synthesis of the optically active modifications of terpineol." By Kenneth Fisher and William Henry Perkin, jun.

The authors have synthesised *d*- and *l*-terpineol from the esters of the *d*- and *l*-modifications of 1-methyl-Δ^1-*cyclo*hexene-4-carboxylic acid, $CMe\begin{matrix}<\\<\end{matrix}\begin{matrix}CH{-}CH_2\\CH_2{\cdot}CH_2\end{matrix}\begin{matrix}>\\>\end{matrix}CH{\cdot}CO_2H$, and have attempted to convert them into the optically active modifications of limonene.

232. "Experiments on the synthesis of the terpenes. Part XIII. Synthesis of *iso*carvestrene ($\Delta^{6:8(9)}$-*m*-menthadiene) and its derivatives." By Kenneth Fisher and William Henry Perkin, jun.

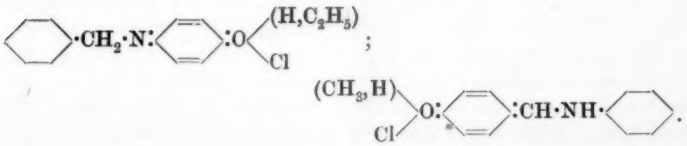
The authors have synthesised 1-*methyl*-Δ^6-cyclo*hexene*-3-*carboxylic acid*, and have converted it into *dihydro*iso*carvestrenol* (I) and iso*carvestrene* (II):

$$CH\begin{matrix}<\\<\end{matrix}\begin{matrix}CMe{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}\begin{matrix}>\\>\end{matrix}CH{\cdot}CMe_2{\cdot}OH \qquad (I.)$$

$$CH\begin{matrix}<\\<\end{matrix}\begin{matrix}CMe{\cdot}CH_2\\CH_2{-}CH_2\end{matrix}\begin{matrix}>\\>\end{matrix}CH{\cdot}CMe{:}CH_2. \qquad (II.)$$

233. "Colour and constitution of azomethine compounds. Part II." By Frank George Pope and Robert Fleming.

The simplest hydroxyazomethine compounds and their ethers are colourless substances, but their hydrochlorides, which are formed by passing hydrogen chloride into benzene solutions of the azomethines, show absorption in the blue and violet region of the visible spectrum. Consequently, it seems necessary to conclude that the salts formed by the action of mineral acids on the azomethines possess a different structure from the azomethines themselves, and it appears most rational to regard them as oxonium salts, thus:



234. "Aromatic arsonic acids." By Marmaduke Barrowcliff, Frank Lee Pyman and Frederic George Percy Remfry.

Sodium *bis*-2-aminotolyl-5-arsinate described by Pyman and Reynolds (*Trans.*, 1908, **93**, 1180) is of little use in trypanosomiasis. The authors have prepared several derivatives of *p*-aminophenylarsonic acid and 2-aminotolyl-5-arsonic acid for possible use in trypanosomiasis; their trypanocidal properties were found to be very slight.

235. "The condensation of salicylaldehyde and benzamide." By Arthur Walsh Titherley and Morris Edgar Marples.

The condensation of salicylaldehyde and benzamide in the presence of sodium acetate produces two isomeric *salicylidenebenzamides*, $HO\cdot C_6H_4\cdot CH{:}N\cdot CO\cdot C_6H_5$, and not the cyclic "coumarazine," $C_6H_4<\begin{matrix}CH{:}N\\ O-CPh\cdot OH\end{matrix}$, described by Cebrian (*Ber.*, 1898, **31**, 1592). The two compounds, which are similar in properties and phenolic in character, were separated by means of acetone.

When condensation between salicylaldehyde and benzamide occurs in presence of hydrogen chloride, wandering of benzoyl occurs, and O-N-N-*tribenzoylsalicylidenediamine*, $BzO\cdot C_6H_4\cdot CH(NHBz)_2$, m. p. 198°, is formed, which is hydrolysed by pyridine and alkali, forming ammonia, benzoic acid, salicylaldehyde, and dibenzamide. The production of the latter shows that a wandering of benzoyl takes place similar to that which occurs in the synthetic formation of the tribenzoyl derivative.

By cautious hydrolysis of the tribenzoyl derivative with cold aqueous alcoholic sodium hydroxide, one benzoyl group is eliminated with the production of N-N-*dibenzoylsalicylidenediamine*,

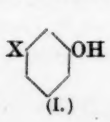
$$HO\cdot C_6H_4\cdot CH(NHBz)_2,$$

m. p. 192°.

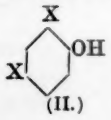
236. "The coumarin condensation." By Arthur Clayton.

A study has been made of the formation of coumarins from substituted phenols and malic acid or ethyl acetoacetate. The following conclusions are drawn:

(1) Phenols of the types shown in formulæ (I) and (II) (where X is an alkyl, hydroxyl, or dialkylamino-group) condense readily with malic acid or ethyl acetoacetate to form derivatives of coumarin:



(I.)



(II.)

(2) Chlorine as a substituent has an effect similar to that of the above groups, but its influence is very much less marked.

(3) The introduction of such substituents as NO_2, CO_2H, and $CO_2{\cdot}C_2H_5$ prevents condensation.

237. "Experiments on the synthesis of 1-methyl*cyclo*hexylidene-4-acetic acid." Part II. By Victor John Harding, Walter Norman Haworth, and William Henry Perkin, jun.

The authors bring forward evidence which, in their opinion, clearly proves that the acid of melting point 41°, obtained by Marckwald and Meth (*Ber.*, 1906, **39**, 1171) by the elimination of water from 4-hydroxy-1-methyl*cyclo*hexyl-4-acetic acid,

$$CHMe\begin{<}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{>}C(OH){\cdot}CH_2{\cdot}CO_2H,$$

is 1-methyl-Δ^3-*cyclo*hexene-4-acetic acid,

$$CHMe\begin{<}CH_2{-}CH\\CH_2{\cdot}CH_2\end{>}C{\cdot}CH_2{\cdot}CO_2H,$$

and not, as the above investigators claim to have established, 1-methyl-*cyclo*hexylidene-4-acetic acid,

$$CHMe\begin{<}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{>}C{:}CH{\cdot}CO_2H.$$

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Avogadro, *Amedeo.* Sur la densité des corps solides et liquides comparée avec la grosseur de leurs molécules, et avec leurs nombres affinitaires. Mémoire I et II. [Mem. Accad. Sci. Torino. XXX, 1824, pp. 81—154. XXXI, 1824, pp. 1—94.] (*Reference.*)
From Professor J. Emerson Reynolds.

Bayliss, *W. M.* The nature of enzyme action. [Monographs of biochemistry.] pp. x + 90. London 1908. (*Recd.* 23/10/08.)
From the Publishers: Messrs. Longmans, Green & Co.

Beadle, *Clayton.* Chapters on papermaking. Vol. V. Concerning the theory and practice of beating. pp. viii + 182. ill. London 1908. (*Recd.* 22/10/08.) From the Author.

Berthelot, *M.* Explosives and their power. Translated and condensed from the French of M. Berthelot by *C. Napier* **Hake** and *William* **Macnab.** pp. xi + 563. ill. London 1892. (*Recd.* 5/8/08.)
From William Macnab, Esq.

Blanchard, *Arthur A.* Synthetic inorganic chemistry. pp. viii + 89. New York 1908. (*Recd.* 30/8/08.)
From the Publishers: Messrs. J. Wiley & Sons.

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Clowes, *Frank.* A treatise on qualitative analysis and practical chemistry. 8th edition. pp. xxiii + 518. London 1908. (*Recd.* 5/6/08.) From the Publishers: Messrs. J. & A. Churchill.

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Curtius, *Theodor,* and **Rissom,** *Johannes.* Geschichte des Chemischen Universitäts-Laboratiums zu Heidelberg seit der Gründung durch Bunsen. Zur Feier der Enthüllung des Bunsendenkmals in Heidelberg. pp. iv + 56. ill. (*Recd.* 1/9/08.) From Geh. Rat Prof. Dr. Curtius.

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Hinds, *J. I. D.* Inorganic chemistry. With the elements of physical and theoretical chemistry. 2nd edition. pp. viii + 651. ill. New York 1908. (*Recd.* 29/10/08.) From the Author.

Holleman, *Arnold Frederick.* A textbook of inorganic chemistry. 3rd English edition, issued in co-operation with *Hermon Charles* **Cooper.** pp. viii + 502. ill. New York 1908. From the Publishers: Messrs. John Wiley & Sons.

Jurisch, *Konrad W.* Saltpeter und sein Ersatz. pp. viii + 356. ill. Leipzig 1908. (*Recd.* 29/6/08.) From the Author.

Le Chatelier, *Henry.* Leçons sur le carbone, la combustion, le lois chimique. pp. xiv + 456. ill. Paris 1908. (*Recd.* 12/8/08.) From the Author.

Lister Institute of Preventive Medicine. Collected papers. No. 4. London 1907. (*Reference.*) From the Director.

London, University of. The Libraries of London: a guide for students. Prepared on the instruction of the Senate of the University of London by *Reginald Arthur* **Rye.** pp. 90. London 1908. (*Reference*). From the University.

Lunge, *George.* [*Editor.*] Technical methods of chemical analysis. English translation from the latest German edition, adapted to English conditions of manufacture, edited by *Charles Alexander* **Keane.** Vol I, in two parts. pp. xxiv + 996. ill. London 1908. (*Recd.* 10/10/08.) From Dr. C. A. Keane.

RESEARCH FUND.

A Meeting of the Research Fund Committee will be held in December next. Applications for Grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on, or before, Monday, December 7th, 1908.

All persons who received Grants in December, 1907, or in December of any previous year, whose accounts have not been declared closed by the Council, are reminded that reports must be in the hands of the Hon. Secretaries not later than Tuesday, December 1st.

The Council wish to draw special attention to the fact that the income arising from the donation of the Worshipful Company of Goldsmiths is to be more or less especially devoted to the encouragement of research in Inorganic and Metallurgical Chemistry. Furthermore, that the income due to the sum accruing from the Perkin Memorial Fund is to be applied to investigations relating to problems connected with the Coal-tar and Allied Industries.

At the next Ordinary Meeting on **Thursday**, November **19**th, 1908, at **8.30** p.m., the following papers will be communicated:

"Meteloidine: a new solanaceous alkaloid." By F. L. Pyman and W. C. Reynolds.

"The affinity of certain alkaloids for hydrochloric acid." By V. H. Veley.

"The affinity constants of bases as determined by methyl-orange." By V. H. Veley.

"The relation between absorption spectra and chemical constitution. Part XII. Some amino-aldehydes and -ketones of the aromatic series." By E. C. C. Baly and Miss E. G. Marsden.

"Organic derivatives of silicon. Part VIII. The resolution of *dl*-sulphobenzylethyl*iso*butylsilicyl oxide, and the properties of the optically active acids." By B. D. W. Luff and F. S. Kipping.

"Study of the constitution and properties of the rhodanides of inorganic radicles. Part I." By A. E. Dixon and J. Taylor.

"The action of phosphorus pentachloride on the methylene ethers of catechol derivatives. III. The cyclic carbonates of dichloro-ethyl- and propyl-catechol." By G. Barger.

"The synthesis of thionaphthen derivatives from styrenes and thionyl chloride." By G. Barger and A. J. Ewins.

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Issued 28/11/08

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 24 No. 347.

Thursday, November 19th, 1908, at 8.30 p.m., SIR WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

The PRESIDENT announced that the Society had become indebted to Professor J. Emerson Reynolds, F.R.S., for presenting a bust of Michael Faraday.

Certificates were read for the first time in favour of Messrs.:

Arthur Clayton, B.Sc., 35, Sisters Avenue, Clapham Common, S.W.
John Charles Jesser Coope, Bulawayo, Rhodesia, S. Africa.
Arthur Gordon Francis, B.Sc., 50, Whitbread Road, Brockley, S.E.
Ross Aiken Gortner, M.A., B.Sc., Lincoln, Nebraska, U.S.A.
Frank Higson, Ivy Bank, Castle Street, Haulgh, Bolton.
James Henry Hoseason, Alderside, Timperley, Cheshire.
Ralph Hough, 14, Longford Place, Victoria Park, Manchester.
Percy May, 126, Cazenove Road, Stamford Hill, N.
Frank George Pope, 28, Alcester Crescent, Upper Clapton, N.E.
Philip John Sageman, 160, Brecknock Road, N.

Certificates have been authorised by the Council for presentation to ballot under Bye-law I (3) in favour of Messrs.:

Thomas Boles Allen, M.A., Medical Faculty, McGill University, Montreal.
Maung Ba, B.A., Rangoon College, Rangoon.
Prince Mom Chow Bhunsri, Saranrome Palace, Bangkok, Siam.
Maung San U, Government Laboratory, Rangoon.

Herbert M. Shilstone, B.Sc., 410, South Front Street, New Orleans, U.S.A.

Rev. John Watt, M.A., Scottish Churches College, Calcutta.

Of the following papers, those marked * were read:

*238. "Meteloidine: a new solanaceous alkaloid."
By Frank Lee Pyman and William Colebrook Reynolds.

Datura meteloides yields 0·4 per cent. of total alkaloid, from which 0·13 per cent. of hyoscine, 0·03 per cent. of atropine, and 0·07 per cent. of a new alkaloid, *meteloidine*, have been obtained.

Meteloidine, $C_{13}H_{21}O_4N$, crystallises in tabular needles, melting at 141—142°. It forms crystalline salts, of which the *hydrobromide*, $C_{13}H_{21}O_4N,HBr,2H_2O$ (needles, m. p. 250°), *aurichloride*,

$$C_{13}H_{21}O_4N,HAuCl_4,\tfrac{1}{2}H_2O$$

(hexagonal plates, m. p. 149—150°), and *picrate* (hexagonal plates, m. p. 177—180°) have been prepared. It is optically inactive, and has no marked physiological action.

It is readily hydrolysed by hot aqueous barium hydroxide, with the formation of tiglic acid and a new base, *teloidine*, according to the equation: $C_{13}H_{21}O_4N + H_2O = C_5H_8O_2 + C_8H_{15}O_3N$.

Teloidine crystallises from moist acetone in needles, which contain one molecule of water of crystallisation, and, after drying at 120°, melts at 168—169°. It forms crystalline salts, of which the *hydrochloride*, $C_8H_{15}O_3N,HCl$ (prisms, m. p. above 300°), *hydrobromide*, $C_8H_{15}O_3N,HBr$ (hexagonal plates, m. p. 295°), and *aurichloride*, $C_8H_{15}O_3N,HAuCl_4,\frac{1}{2}H_2O$ (hexagonal plates, m. p. 225°) have been characterised.

Attention was drawn to the similarity of the properties of teloidine with those of tropine and oscine.

*239. "The affinity of certain alkaloids for hydrochloric acid."
By Victor Herbert Veley.

Determinations have been made of the affinity values of the nitrogen atoms or amino-groups of certain alkaloids, which, although containing more than one atomic proportion of nitrogen, yet form stable combinations with one molecular proportion of hydrogen chloride, the dihydrochlorides being produced only under special conditions, or not, as yet, having been obtained. It was shown by the application of the methyl-orange method that in all cases the affinity values of these amino-groups are of a widely different order.

In the case of the cinchona alkaloids, the affinity value of one amino-group is rather less than that of a hydropyridine, whilst that of the other is rather lower than that of quinoline. These results are in accordance with the accepted constitution of these alkaloids and the thermo-neutrality values obtained by addition of one and two molecular proportions of hydrogen chloride respectively.

In the case of pilocarpine, the value of one grouping is intermediate between that of ammonia and the limit value of the methyl-orange method, whilst that of the other is equal to those of true amphoteric electrolytes.

A methylglyoxaline was examined on account of the relationship of pilocarpine to these compounds; the value of the two amino-groups and its general behaviour correspond with a diamino-base of the type of hydrazine.

Of the *Nux Vomica* alkaloids, strychnine and brucine were examined; in both cases, the affinity value of one amino-group was beyond the limit value of the methyl-orange method, whilst that of the other corresponded with the betaines, which is in accordance with the views held regarding their constitution.

Discussion.

Dr. Veley, in reply to Dr. Jowett, stated that so far as results had been obtained it appeared probable that if an alkaloid was constituted of two residues, either or both containing an amino-group, the affinity value of the one was affected by that of the other.

This had been observed more especially in the case of tropine, the parent base of the atropine and cocaine alkaloids, the results for which it was hoped shortly to communicate to the Society.

***240. "The relation between absorption spectra and chemical constitution. Part XII. Some amino-aldehydes and -ketones of the aromatic series." By Edward Charles Cyril Baly and Effie Gwendoline Marsden.**

The absorption spectra of *o*- and *p*-aminobenzaldehyde and the three isomeric aminoacetophenones have been observed; they all exhibit a single broad absorption band which is within the visible region of the spectrum, so that the substances are visibly coloured. The addition of a small quantity of alcoholic hydrochloric acid to the solution of each of the compounds causes a considerable deepening of the colour, which is due to the formation of a new absorption band nearer to the red than the principal band referred to above. This phenomenon does not occur in aqueous solution, and is most evident with the para-

isomeride and least with the meta. It has also been observed in the case of tetramethyldiaminobenzophenone and the aminobenzaldoximes. The phenomenon is apparently due to an increased activity of the amino-group, and hence affords an explanation of the catalytic action of mineral acid on the acetylation of amino-compounds.

DISCUSSION.

Dr. HEWITT inquired if the absorption spectrum of *p*-aminobenzaldehyde in presence of a small quantity of hydrochloric acid was measured in absolute alcoholic solution, and he also wished to know how the substance was isolated in a pure condition.

Mr. BALY, in reply to Dr. Lowry, said that the original compound was restored when the acid was neutralised. In reply to Dr. Forster: the absorption spectrum of the hydrochloride was entirely different from that of the base in presence of a trace of alcoholic hydrogen chloride. Considerable difficulty had been experienced in the preparation of *p*-aminobenzaldehyde. It was obtained from *p*-aminobenzaldoxime and then regenerated from its hydrochloride. The melting point was correct, and, moreover, the condensation product was very different from the aminobenzaldehyde itself in that it was only very slightly soluble in alcohol.

***241. "Organic derivatives of silicon. Part VIII. The resolution of *dl*-sulphobenzylethyl*iso*butylsilicyl oxide and the properties of the optically active acids." By Bernard Dunstan Wilkinson Luff and Frederic Stanley Kipping.**

dl-*Sulphobenzylethylisobutylsilicyl oxide*,

$$[SO_3H\cdot C_6H_4\cdot CH_2\cdot SiEt(C_4H_9)]_2O,$$

is resolved into its optically active components by the fractional crystallisation of its salt with *d*-methylhydrindamine; the pure *d*A*d*B-salt obtained melts at 207—209°, and has $[\alpha]_D + 16{\cdot}7°$ in methyl-alcoholic solution. The specific rotation of the sodium salt of the *d*-acid is $[\alpha]_D + 10{\cdot}4°$. The pure *l*A*l*B-salt (melting at 207—209° and having $[\alpha]_D - 17{\cdot}0°$ in methyl-alcoholic solution) is obtained by fractionally crystallising the salt of the *dl*-acid with *l*-methylhydrindamine; the specific rotation of the sodium salt of the pure *l*-acid is $[\alpha]_D - 10{\cdot}5°$.

d-*Methylhydrindamine* l-*sulphobenzylethylisobutylsilicyl oxide* and the corresponding *d*A*l*B-salt, prepared by combining the optically pure acids with *d*- and *l*-methylhydrindamine respectively, are oils at the ordinary temperature.

l *Menthylamine* d-*sulphobenzylethylisobutylsilicyl oxide* crystallises

well (with $4H_2O$), melts when anhydrous at 254—258°, and its specific rotation in methyl-alcoholic solution is $[\alpha]_D - 13{\cdot}9°$. The salt of the *l*-acid is very similar in properties, but melts at 253—257°, and has $[\alpha]_D - 17{\cdot}2°$ in methyl-alcoholic solution. The salt of the *dl*-acid melts at 240—245°, and has $[\alpha]_D - 14{\cdot}7°$.

d-*Bornylamine* d-*sulphobenzylethylisobutylsilicyl oxide* melts at 209—211°; the salt of the *l*-acid melts at 210—212°.

Cinchonidine d-*sulphobenzylethylisobutylsilicyl oxide* crystallises in needles melting at 171—173°, whereas the salt of the *l*-acid melts at 181—183°; the specific rotations of the two salts, however, are practically identical, having the values $[\alpha]_D - 68{\cdot}5°$ and $[\alpha]_D - 69{\cdot}3°$ respectively in methyl-alcoholic solution. The *cinchonidine hydrogen* salts of the *d*- and *l*-acids are crystalline, and decompose at 232—234° and 229—231° respectively.

***242. "The action of phosphorus pentachloride on the methylene ethers of catechol derivatives. Part III. The cyclic carbonates of dichloro-ethyl- and -propyl-catechol." By George Barger.**

From α-3 : 4-*methylenedioxyphenyl-αβ-dichloroethane*,

$$CH_2\langle{}^{O}_{O}\rangle C_6H_3{\cdot}CHCl{\cdot}CH_2Cl,$$

b. p. 159—160°/12 mm., or from the corresponding *chlorohydrin*,

$$CH_2\langle{}^{O}_{O}\rangle C_6H_3{\cdot}CH(OH){\cdot}CH_2Cl,$$

m. p. 95°, b. p. 169—170°/7 mm., the very unstable, crystalline *substance*, $CCl_2\langle{}^{O}_{O}\rangle C_6H_3{\cdot}CHCl{\cdot}CH_2Cl$, m. p. 56°, b. p. 170—174°/6 mm., was obtained; the latter is transformed by formic acid into the cyclic *carbonate*, $O{:}C\langle{}^{O}_{O}\rangle C_6H_3{\cdot}CHCl{\cdot}CH_2Cl$, b. p. 180—182°/8 mm. Similarly, from *iso*safrole dichloride, the *substances*,

$$CCl_2\langle{}^{O}_{O}\rangle C_6H_3{\cdot}CHCl{\cdot}CHCl{\cdot}CH_3,$$

b. p. 174·5—175·5°/8 mm., and $O{:}C\langle{}^{O}_{O}\rangle C_6H_3{\cdot}CHCl{\cdot}CHCl{\cdot}CH_3$, b. p. 186—189°/8 mm., were obtained. The cyclic carbonates are readily hydrolysed to catechol derivatives, but the latter are so unstable that they have not as yet been obtainable in the pure state.

***243. "The synthesis of thionaphthen derivatives from styrenes and thionyl chloride." By George Barger and Arthur James Ewins.**

When styrene halides or allied derivatives are heated with a large excess of thionyl chloride to 180—270°, sulphur compounds result, which

are most probably derivatives of thionaphthen. More or less extensive chlorination always takes place; thus $\alpha\beta$-dibromostyrene,

$$C_6H_5\cdot CHBr\cdot CH_2Br,$$

yields *hexachlorothionaphthen*, C_8Cl_6S, m. p. 158°. A number of similar derivatives from other styrenes were described.

244. "The affinity constants of bases as determined by the aid of methyl-orange." By Victor Herbert Veley.

It was shown that the methyl-orange method, as described in a previous communication (*Trans.*, 1908, **93**, 652, *et. seq.*), gives results which are concordant with those obtained by the catalysis of methyl-acetate, inversion of sucrose, and electric conductivity methods. If the last named give accurate results, then the same applies equally to the first, which possesses the advantages of simplicity of apparatus, brevity, and smaller amount of material required.

Determinations have been made of the hydrolysis and affinity constant values of about 50 cyclic bases derived from benzene, pyridine, naphthalene, and quinoline; the mutual relationship and effects produced by the substitution of one or more atomic proportions of hydrogen, whether in the nucleus or side-chain, by various elements or groupings were discussed.

The variation of the several constants, namely, $C_{(H)}$, K_w, and K_b, with temperature was dealt with, and it was shown that in cases in which determinations of these constants have been made by the same or different trustworthy methods, the experimental results obtained are in accordance with those calculated by the formula $K_{T_1}/K_T = (T_1/T)^m$ (T = absolute temperature). Thus ionic dissociation, whether of water or electrolytes, cannot be differentiated in respect of temperature from any other change, generally regarded, as of a purely chemical nature. The importance of this formula for the purpose of other calculations was also emphasised.

245. "Study of the constitution and properties of the rhodanides of inorganic radicles." By Augustus Edward Dixon and John Taylor.

The mean refraction value of the ·NCS group in organic thiocarbimides being about 28·1, as calculated from the formula

$$M_D = \frac{(\mu_D - 1)p}{dt°/4°},$$

whilst that for the ·SCN group in various organic thiocyanates is about 23·3, the authors, by measuring the molecular refraction of the

rhodanides, $P(CNS)_3$ and $PO(CNS)_3$, have endeavoured to ascertain the refraction effect of the rhodanic groups in these substances, with the object of deciding whether the groups have the configuration ·NCS or ·SCN.

The number found for the rhodanic group (assuming the three to be of equal value) being in each case near to 28, the authors conclude that, so far as the results of this purely physical method may be relied on as affording trustworthy evidence with respect to the atomic linking, the two rhodanides mentioned have the thiocarbimidic constitutions $P(\cdot NCS)_3$ and $PO(\cdot NCS)_3$ respectively.

Phosphoryl trithiocarbimide yields definite additive compounds with one and with two molecular proportions of aniline, or with one of diphenylamine, the products being nearly insoluble in cold water. By prolonged contact with cold water, by treatment with hot water, or by dissolution in aqueous alcohol, they are hydrolysed, yielding one-third of the contained sulphur as substituted thiocarbamide, and two-thirds as free or combined thiocyanic acid. Phosphorus trithiocarbimide (1 mol.), like the phosphoryl analogue, is precipitated completely from benzene solution by one molecular proportion of aniline; the solid product, when dissolved in cold alcohol, gives the reactions of a thiocarbamide, and is hydrolysed readily into one molecule of phenylthiocarbamide and two molecules of thiocyanic acid. The authors suggest that very pronounced electropositive or electronegative character in the inorganic radicle may have power to influence the configuration of the rhodanic group with which it is associated.

246. "The electrical conductivity of phosphoric acid." By Harry Edward William Phillips.

Pure phosphoric acid was prepared by treating redistilled phosphorus trichloride with specially purified water at an equable temperature, and oxidising the resulting phosphorous acid by means of pure nitric acid. The hydrochloric acid and the excess of nitric acid were then expelled by heat.

The phosphoric acid thus prepared was a transparent, colourless oily liquid, which showed no tendency to crystallise in the higher strengths, but a specimen of 43 per cent. solution yielded numerous small, soft, gelatinous crystals spontaneously on cooling. The pure acid neither reddened litmus nor decomposed carbonates.

For the measurement of conductivity, Kohlrausch's telephone method was employed, and a special Wheatstone bridge was made by the author for the purpose, which gave opportunity of very accurate work.

Curves were drawn showing the actual conductivity per cent. of the acid at 0°, also a set of curves showing the comparative conductivity per cent. of sulphuric, nitric, hydrochloric, and phosphoric acids and sodium and potassium hydroxides. The results obtained were also worked out to molecular conductivities, and these were compared with the nine values previously obtained by Kohlrausch at 18°, and the more extended work of Jones and Bassett at 0°; they were also compared with the corresponding values for the three common mineral acids. Finally, curves of dissociation values, obtained by means of the formula $\frac{\Lambda}{\Lambda_\infty}$, were drawn.

The results seem to bear out the theory of indicators regarding the ionisation of the hydrogen atom in the molecule of phosphoric acid.

247. "The molecular volumes of the nitrites of barium, strontium, and calcium." By Prafulla Chandra Rây.

The molecular volumes of the nitrites of barium, strontium, and calcium in their monohydrated forms are 77·87, 74·59, and 67·24, whilst those of the anhydrous salts are 70·90, 62·54, and 57·56 respectively. The radicle NO_2 of the anhydrous nitrites of these metals occupies a constant volume, namely, 24·2.

248 "The formation of some carbides." By John Norman Pring.

An investigation has been made of the direct union of carbon with the elements aluminium, silicon, and iron in the absence of solid and gaseous impurities. Some preliminary experiments were also carried out with magnesium.

An intimate mixture of the metal with highly-purified carbon, both in a very fine state of division, was heated in a suitable apparatus, enabling definite constant temperatures to be maintained over long intervals, and capable of being evacuated to a pressure below 0·01 mm.

The direct union of pure silicon and carbon in a vacuum commences between 1250° and 1300°, and the presence of iron does not apparently facilitate the reaction, nor does carbon monoxide exert any influence between the limits of atmospheric pressure and 0·03 mm.

Aluminium unites directly with pure carbon in a vacuum at its melting point (650°), forming aluminium carbide, Al_4C_3, and the velocity of the reaction increases with the temperature, proceeding rapidly above 1400°.

Iron unites directly with carbon at about 700° under a pressure of about 0·05 mm.

Magnesium shows evidence of forming a new carbide below 600°, this compound giving some saturated hydrocarbon on decomposition with water or acids.

249. "4-Chloroacenaphthene."

By Holland Crompton and Eva Richardis Cyriax.

When acenaphthene in chloroform solution is treated with chlorine (1 mol.) and the solvent evaporated, an oil remains which does not crystallise on standing and from which no crystalline product could be obtained by means of solvents. On distillation, it yields some unchanged acenaphthene, and then, as main product, a distillate passing over at 305—310° which solidifies in the receiver. This consists of almost pure 4-chloroacenaphthene.

4-*Chloroacenaphthene* crystallises from alcohol in colourless leaflets; it melts at 65°, and boils at 309°; its *picrate* crystallises in yellow needles, melting at 133°. On oxidation by sodium dichromate in acetic acid solution, it yields a chloronaphthalic acid, the anhydride of which melts at 198° and the imide at 278°. When the calcium salt of this acid is heated with soda-lime, naphthalene is obtained, mixed with a little α-chloronaphthalene. If the copper salt is used in place of the calcium salt, α-chloronaphthalene is produced with little naphthalene. On fusing with potassium hydroxide at 250—260°, the acid is converted into 4-hydroxynaphthalic acid, the anhydride of which melts at 257°; this acid had previously been obtained by Graebe from 4-bromonaphthalic acid (*Annalen*, 1903, **327**, 77). The formation of this 4-hydroxynaphthalic acid and of α-chloronaphthalene show that the acid is 4-chloronaphthalic acid, and confirm the constitution given to the chloroacenaphthene.

250. "Some molecular compounds of styphnic and picric acids."

By Charles Stanley Gibson.

The following compounds have been prepared:

Acenaphthene styphnate, $C_{12}H_{10},C_6H(OH)_2(NO_2)_3$, crystallising in long, orange-coloured prisms melting at 153—154°; *phenanthrene styphnate*, $C_{14}H_{10},C_6H(OH)_2(NO_2)_3$, crystallising in yellowish-red needles melting at 125—126°; *bromonaphthalene styphnate*, $C_{10}H_7Br,C_6H(OH)_2(NO_2)_3$, crystallising in small, bright yellow needles melting at 107—108°; m-*nitroaniline styphnate*, $NH_2{\cdot}C_6H_4(NO_2),C_6H(OH)_2(NO_2)_3$, crystal-

lising in pale yellow needles melting at 137°; and m-*nitroaniline picrate*, $NH_2 \cdot C_6H_4(NO_2), C_6H_2(OH)(NO_2)_3$, crystallising in yellow, radiating needles melting at 143°.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Manchester, City of, *Rivers Department.* Annual Report for the year ending March 25th, 1908. Manchester 1908. (*Recd.* 21/10/08.) From the Rivers Committee.

Metropolitan Water Board. First report on research work by *A. C.* **Houston,** on the vitality of the typhoid bacillus in artificially infected samples of raw Thames, Lee, and New River water, with special reference to the question of storage. pp. 32. [London 1908.]

——— Reports of Committees. [pp. i—xxxv. Report on the results of the chemical and bacteriological examination of the London waters for the twelve months ending 31st March, 1908, by *A. C.* **Houston.**] pp. 31 + xxxv. [London 1908.] (*Recd.* 23/7/08.) From the Metropolitan Water Board.

Meyer, *H.*, and **Tingle,** *J. Bishop.* Determination of radicles in carbon compounds. 3rd edition. pp. xiv + 218. New York 1908. (*Recd.* 11/7/8.) From the Publishers: Messrs. John Wiley & Sons.

Parry, *L.* The analysis of ashes and alloys. pp. iv + 143. London 1908. (*Recd.* 30/8/08.) From the Publishers: "The Mining Journal."

Società Italiana per il Progresso delle Scienze. Atti. Prima riunione, Parma, Settembre 1907. pp. xxiii + 325. Roma 1908. (*Reference.*) From the Society.

Society of Chemical Industry. Decennial index of the Journal of the Society of Chemical Industry. Vols. XV to XXIV, 1896—1905. Part II, Index of Subjects. Compiled by *F. W.* **Renaut.** pp. 552. London 1908. (*Reference.*) From the Society.

Sykes, *Walter J.* The principles and practice of brewing. 3rd edition, thoroughly revised by the Author and *Arthur R.* **Ling.** pp. xviii + 588. ill. (*Recd.* 31/7/08.) From Arthur R. Ling, Esq.

Tschirch, *A.* Chemie und Biologie der pflanzlichen Sekrete. pp. 95. Leipzig 1908. (*Recd.* 30/8/08.) From the Author.

Zeitschrift für physiologische Chemie. Edited by *F.* **Hoppe-Seyler.** Vols. VI, VII, and parts 1 to 5 of Vol. VIII. Strassburg 1882—84. (*Circulating.*) From J. Parry Laws, Esq.

II. *By Purchase.*

Angeli, *Angelo.* Ueber einige sauerstoffhaltige Verbindungen des Stickstoffs. Uebersetzt von *Kurt* **Arndt.** (Sammlung, XIII). Stuttgart 1908.

Brand, *Kurt.* Die elektrochemische Reduktion organischer Nitrokörper und verwandter Verbindungen. (Sammlung, XIII). Stuttgart 1908.

Fischer, *A.* Elektroanalytische Schnellmethoden. Elektroanalyse unter Bewegen von Elektrolyt oder Elektrode. (Die chemische Analyse, Vols. 4 and 5.) pp. 304. (*Recd.* 20/6/08.)

[**Grasshoff,** *Johann.*] Philosophia Salomonis oder: Geheimes Cabinet der Natur und Kunst des Weisen Königes Salomons eröffnet durch den sogenannten grossen und kleinen Bauer wahren Besitzern des königlichen Steins. pp. [xvi] + 207. Augsburg 1753. (*Reference.*)

Groth, *Paul.* Chemische Krystallographie. Teil II. Die anorganischen Oxo- und Sulfosalze. pp. viii + 914. ill. Leipzig (*Recd.* 29/10/08.)

Handbuch der anorganisch Chemie. Edited by *R.* **Abegg** and *Fr.* **Auerbach.** Vol. II. Part 1. pp. xiii + 867. Leipzig 1908. (*Reference.*)

Hollandus, *Isaac.* Curieuse und rare chymische Operationes, worinnen nicht allein einige bisshero unbekannte Geheimnisse die rechte Universal-Tinctur zu erlangen, angezeigt; besondern das Fundament aller solcher Operationen, so in Ausziehung des Saltz und Oels aus denen Mineris bestehet, auf eine gar deutliche Weise gezeiget wird . . . Aus einem alten Autographo MSCto des Autoris heraus gegeben von R. H. C. pp. [xvi] + 400. Leipzig 1714.

Mackenzie, *Colin.* One thousand experiments in chemistry; with illustrations of natural phenomena; and practical observations of the manufacturing and chemical processes at present pursued in the successful cultivation of the useful arts. A new edition. pp. vi + 30 + v to xxxii + 646. ill. London 1822.

Schmidt, *Julius.* Die organischen Magnesiumverbindungen und ihre Anwendung zu Synthesen. II. (Sammlung, XIII). Stuttgart 1908.

Skrabal, *A.* Die induzierten Reaktionen, ihre Geschichte und Theorie. Die Reaktion Ferrosalz-Permanganat in salzsaurer Lösung. (Sammlung, XIII). Stuttgart 1908.

Waite, *Arthur Edward.* Lives of alchemystical philosophers, based on materials collected in 1815, and supplemented by recent researches. With a philosophical demonstration of the true principles of the magnum opus, or great work of alchemical re-construction, and some account of the spiritual chemistry. To which is added a bibliography

of alchemy and hermetic philosophy. pp. 315. London 1888. (*Recd.* 12/11/08.)

[**Walchin**, *Dorothea Juliana.*] Das Mineralische Gluten, Doppelter Schlangen-Stab, Mercurius Philosophorum, langer und kurtzer Weg zur Universal-Tinctur. Deutlich und klärlich entdecket und angewiesen durch D. I. W. von Weimar aus Thüringen. pp. 118. Leipzig 1705. (*Reference.*)

—— Der Philosophische Perl-Baum, das Gewächse der drey Principien, zu deutlicher Erklärung des Steins der Weisen, wie er mit seinen Wurtzeln in der äusern und finstern Welt, mit seiner Blüthe aber in der Paradisischen- und Licht-Welt, und mit seiner reiffen Frucht in der Englischen und Himmlischen Welt stehet und wächset. Bescrieben durch D. I. W. von Weimar aus Thüringen. pp. 189. Leipzig 1705. (*Reference.*)

—— Schlüssel zu dem Cabinet der geheimen Schatz-Kammer der Natur, zur Such- und Findung des Steins der Weisen, durch Fragen und Antwort gestellet. Verfertiget und der Welt gezeiget durch D. I. W. von Weimar aus Thüringen. pp. 288. Leipzig 1706. (*Reference.*)

RESEARCH FUND.

A Meeting of the Research Fund Committee will be held in December next. Applications for Grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on, or before, Monday, December 7th, 1908.

All persons who received Grants in December, 1907, or in December of any previous year, whose accounts have not been declared closed by the Council, are reminded that reports must be in the hands of the Hon. Secretaries not later than Tuesday, December 1st.

The Council wish to draw special attention to the fact that the income arising from the donation of the Worshipful Company of Goldsmiths is to be more or less especially devoted to the encouragement of research in Inorganic and Metallurgical Chemistry. Furthermore, that the income due to the sum accruing from the Perkin Memorial Fund is to be applied to investigations relating to problems connected with the Coal-tar and Allied Industries.

At the next Ordinary Meeting on **Thursday,** December 3rd, 1908, at 8.30 p.m., there will be a ballot for the election of Fellows, and the following papers will be communicated:

"Double salts of potassium iodide with mercury iodide and camphor dimercuriodide in organic solvents." By J. E. Marsh and R. de J. Fleming-Struthers.

"Action of mercuric iodide on ketones in alkaline solution." By J. E. Marsh and R. de J. Fleming-Struthers.

"Condensation of camphor with mercuric iodide." By J. E. Marsh and R. de J. Fleming-Struthers.

"The relation between absorption spectra and chemical constitution. Part XIII. Some Pyrones and allied compounds." By E. C. C. Baly, J. N. Collie, and H. E. Watson.

"Organic derivatives of arsenic. Part I. Dicamphorylarsinic acid." By G. T. Morgan and Miss F. M. G. Micklethwait.

"Tellurium dicyanide." By H. E. Cocksedge.

"Boron thiocyanate." By H. E. Cocksedge.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those whose sign from "General Knowledge" are printed in *italics*.

The following Candidates have been proposed for election. A ballot will be held on Thursday, December, 3rd, 1908.

Akers, Noel Charles,

26, King's Avenue, Muswell Hill, London, N.

At present Senior Student, Junior Demonstrator, of Chemistry at City and Guilds Technical College, Finsbury. Trained at City and Guilds Technical College, Finsbury. Obtained Certificate of above. Now Senior Student, Junior Demonstrator at above. Intermediate Associate of Institute of Chemistry exam.

R. Meldola.	Edward W. Bealey.
John Castell-Evans.	J. Mello Wadmore.
Leslie H. Berry.	Chas. R. Darling.

Aubertin, Thomas,

George Anderson & Co. (1905), Ltd., Carnoustie, N. B.

Chemist to the above and to Grice's Gas Engine Co., Ltd., the two firms working in conjunction. B.A. Oxford. Honours in Chemistry, Final Examination, 1907, and wish to keep in touch with the progress of chemistry.

Andrea Angel.	H. B. Baker.
Allan F. Walden.	W. T. Grice.
J. E. Marsh.	Douglas Berridge.

D. L. Chapman.

Baker, Thomas James,

Trebarwith, Chester Road, Erdington, near Birmingham.

Senior Science Master in King Edward's High School, Birmingham. D.Sc. (London) in Chemistry; late Granville Scholar of London University. B.Sc. (Birmingham) late Tangye Scholar in Chemistry, Mason Coll., Birmingham. Science Master since 1888 in King Edward's School, Birmingham, teaching Chemistry and Physics. Lecturer on Chemistry in the Bilston Technical School since 1897.

Author of "The Thermo-chemistry of the Alloys of Copper and Zinc." Philosopical Transactions of the Royal Society, 1901, Vol. 196. Joint Author of "Note on the Electro-Deposition of Brass," *Chemical News*, July 28, 1899.

William A. Tilden. T. Slater Price.
Percy F. Frankland. Alex. Findlay.
Lionel M. Jones.

Barrett, Maurice,

Holly Bush, Headingley, Leeds.

Technical Chemist. Five years' research work in ceramics. Method for determining the fusibility of glaze silicates. Production of opalescent glazes at high temperatures. Further development of avenlinine glazes. Development of multi-coloured *salt* glazes. Investigation on the production of true malt glazes. Assoc. American Ceramic Society, Memb. English Ceramic Society, Memb. American Chemical Society, &c.

F. W. Branson. J. W. Mellor.
Thomas Fairley. *J. H. Gough.*
B. A. Burrell.

Bickerstaffe, Robert,

Chilterns, Wooburn Green, Bucks.

Works Chemist at Messrs. Thomas and Green, Ltd., Paper Makers, Wooburn Green, Bucks. I have had a 3 years' course in Faculty of Technology, Victoria University, Manchester, in Applied Chemistry. I obtained the Certificate of the University and the Diploma of School of Technology and Associateship. I am now chemist in the above Paper Works. The course included Organic and Inorganic Chemistry, the Chemical Technology of Papermaking, also Physics and German.

W. J. Pope. L. G. Radcliffe.
Jul. Hübner. F. S. Sinnatt.
Jas. Grant. C. Stanley Gibson.

Birch, William Colet, B.A., A.I.C.,

22, Glazbury Road, West Kensington, London.

Student, King's College, Cambridge. Scholar of King's College, Cambridge. Assistant Demonstrator in the University Chemical Laboratory, Cambridge.

W. J. Sell. F. W. Dootson.
H. O. Jones. H. J. H. Fenton.
Charles T. Heycock.

Brakes, William Sudderick,

137, Steade Road, Sheffield.

Schoolmaster. Educated at University College, Nottingham. At present, first assistant at Norton Lees Higher Elementary School, Sheffield. Am desirous of keeping in touch with the latest Chemical Research.

Herbert Simpson Newbould. A. H. Salway.
Harry J. Unwin. *E. R. Watson.*

F. W. Caton.

Clement, Leonard,

Beamsley, Fairhaven, nr. Lytham, Lancs.

Analyst to the Nelson Sewage Works. Exhibitioner in Natural Science, Sidney Sussex Coll., Cambridge, 1903. Scholar in Natural Science, Sidney Sussex Coll., Cambridge, 1904. Part I. Natural Science Tripos, Cambridge (Second Class), 1905. Part II. Natural Science Tripos, Cambridge (Second Class), 1906. Associate of the Institute of Chemistry, 1908. (Final Examinations in Foods, Drugs and Water.) For 15 months Temporary Assistant Analyst at the Custom House, London.

F. H. Neville. H. O. Jones.
H. J. H. Fenton. Francis Jones.

James Connah.

Cowley, Robert Charles.

College of Pharmacy and Chemistry, Brisbane, Australia.

Director (elect) of above. Formerly Principal of Liverpool School of Pharmacy. Author of "Comments on Alkaloidal Estimations of the British Pharmacopœia." Contributor and joint contributor of numerous papers on general and Pharmaceutical Chemistry.

J. W. Clayton. J. Rymer Young.
W. Hall Jowett. Peter MacEwan.
Edward Davies. *Alfred Smetham.*

William C. R. Kynaston.

Duckworth, Hugh Cecil,

66, Victoria St., Westminster, S.W.

With the 12-Hours Stove Syndicate Ltd., 66, Victoria St., London, S.W. Late Chemist to Messrs. Loders and Nucoline Ltd., Silvertown. Late Student in the Chemical Section of the Central Technical College, South Kensington. (Am desirous of attending Lectures and Papers.)

Henry E. Armstrong. T. Martin Lowry.
William Robertson. Ronald Tonkin.

Edward Horton.

Dunnicliff, Horace Barratt,

39, Herne Hill, London, S.E.

B.A. (Cantab.), B.Sc. (London). Student. First Class Natural Sciences Tripos, Part I., Cambridge, 1906. Second Class Natural Sciences Tripos, Part II. (Chemistry), 1908. B.Sc. (Honours in Chemistry) London University, 1907. Demonstrator (Assistant) of Chemistry in Cambridge University Laboratories, April, 1907, and January, 1908.

H. J. H. Fenton. F. W. Dootson.
W. J. Sell. H. O. Jones.
G. D. Liveing.

Easton, Reginald Freeman,

38, Edith Road, W. Kensington, W.

Educated at St. Paul's School. Studied Chemistry under Professor Meldola, F.R.S., at the City and Guilds Technical College, Finsbury.

R. Meldola. Arthur J. Starey.
John Castell-Evans. B. S. Evans.
F. Henry Streatfeild. *Lawrence Briant.*
Frank Clowes.

Everitt, Charles,

67, Boston Avenue, Southend-on-Sea, Essex.

Staff of the *Encyclopædia Britannica*, 11th ed. Studied chemistry at the East London College under Dr. J. T. Hewitt, M.A., D.Sc., Ph.D., from 1894—1899. Natural Science Demy of Magdalen College, Oxford, 1899—1903; First Class in Honours Mathematical Moderations, 1901; First Class in the Honours Chemistry Finals, 1902; Master of Arts of Oxford.

W. W. Fisher. A. F. Walden.
John Watts. T. S. Moore.
J. E. Marsh. J. T. Hewitt.

Girvan, Arthur Frank,

8, Chatsworth Road, West Norwood, S.E.

Chemist. B.Sc. (Lond.) Hons. Assistant Chemist Royal Commission on Sewage Disposal from Sep. '05 to the present time.

George McGowan. J. N. Collie.
William Ramsay. N. T. M. Wilsmore.
Samuel Smiles.

Green, Henry Hamilton,

36, Princes Square, Regent Park, Glasgow.

Chemistry Assistant—Lecturing, and Analytical Work. Chemistry

Assistant in the West of Scotland Agricultural College for four years. At present Assistant to Prof. Berry, Professor of Chemistry. Advanced student in the laboratories of Glasgow University; Final B.Sc. in process of completion.

R. A. Berry. Charles E. Fawsitt.
T. S. Patterson. Frederick Soddy.
John Ferguson.

Griffin, John,

7, Carlton Terrace, Batley, Yorkshire.

Chemistry Master. Part I and Part II (Chemistry) Science Tripos, Cambridge. Wish to keep up knowledge of Chemistry by means of the publications of the Chemical Society.

F. W. Dootson. H. O. Jones.
W. J. Sell. *R. H. Adie.*
H. J. H. Fenton. *J. Parkin.*

Fairburn, Henry,

Northallerton.

Chemist. Analysis of water, milk, &c., forms a branch of my calling. Member of the Pharmaceutical Society. Student at the Pharmaceutical Society's School; attended 110 lectures on Chemistry under Professor Wyndham R. Dunstan, F.R.S., and 3 hours daily from Octr. to July for Practical Chemistry under Professor Attfield, F.R.S.

John Attfield. Wyndham R. Dunstan.
John C. Umney. Thomas Tyrer.
Chas. Umney. *C. T. Bennett.*

Hebron, John Henry Albert,

9, Buller Street, Derby.

Chemistry Master, Municipal Secondary School, Derby. B.Sc. (Honours in Chemistry, London), 1906; Diploma in Chemistry of Derby Technical College; 7 years Chemistry Master, School of Science, Jarrow-on-Tyne (1895–1902); 6 years Chemistry Master, Municipal Secondary School, Derby (1902–1908).

A. Jamieson Walker. J. A. Smythe.
P. Phillips Bedson. J. W. Patterson.
F. C. Garrett. *J. Archyll Jones.*

Hinks, Edward,

23, Tavistock Road, Croydon.

Analytical Chemist. B.Sc. Lond., F.I.C. Author of contributions to *The Analyst*, 1907, on the detection of cocoanut oil in butter. Public

Analyst (Temporary) for the County of Surrey and the Borough of Reigate.

R. Bodmer. W. C. Ball.
John Wade. Horace Finnemore.

J. H. Ryffel.

Hughes, Joseph Albert,

School of Mines, Charter Towers, Queensland.

Demonstrator in Chemistry and Assaying School of Mines, Charter Towers, Queensland. Student Charter Towers School of Mines, 1901—1905. Senior Demonstrater Chemistry and Assaying at same school from 1906 and still occupy same position. Practical mining and milling experience fifteen years. Hold diploma of Chemist and Assayer of same school.

George J. Saunders. Basil Turner.
J. A. Schofield. C. Walker.

F. B. Guthrie.

Hull, Thomas Ernest,

6, Selborne Terrace, Greenbank, Darlington.

Analytical Chemist. Assistant analytical and metallurgical chemist to the Darlington Forge Co., Ltd. Engaged in microscopical examination of iron and steel. Student at the Darlington Technical College from 1899—1907, having gained a "King's Prize" and success in the Honours Stage, Practical Inorganic Chemistry; also successes in Theoretical Organic and Inorganic Chemistry, Alkali Manufacture, Physiography, Practical Mathematics, Magnetism and Electricity, &c. Obtained Central Evening Scholarship for further study of Organic and Inorganic Chemistry at Armstrong College, Newcastle-on-Tyne (Session 1906—1907). Appointed Teacher in Metallurgy at the Darlington Technical College, Sept., 1907.

P. Phillips Bedson. G. P. Dodds.
F. C. Garrett. *George Dean.*
J. A. Smythe. *F. Henry Streatfeild.*

S. Hoare Collins.

Irvine, James Colquhoun,

Dunmurry Rathelpie St. Andrews.

Lecturer in Organic Chemistry in the United College, University of St. Andrews, Ph.D. (Leipzig), D.Sc. (St. Andrews). Author of twenty-four papers in organic chemistry and biological chemistry. In charge of the Chemical Research Laboratory, St. Andrews.

Thomas Purdie. Alex. Mackenzie.
James Walker. *H. R. LeSueur.*
G. Druce Lander. *M. O. Forster.*

Johnson, Grove,

124, Savoy Court, Strand, W.C..

Brewers' analyst and bacteriologist. "Honours" City and Guilds of London Institute. Discoverer of Saccharomyces Thermantitonum. Author of Paper on above Subject delivered before the "Institute of Brewing," July, 1905. At present writing a work on "Practical Yeast Culture for the use of Students."

Arthur C. Claudet. George T. Holloway.
Harold W. Harman. Alfred Gordon Salamon.
Arthur R. Ling.

Keiller, Patrick Anderson,

Hawkhill House, Dundee.

Analytical Chemist. Chemistry (Higher Standard) B.Sc., St. Andrews University. Three years chief assistant to Mr. Jas. Hendrick, County Analyst, Aberdeen. Twenty months Head Chemist to Messrs. J. & J. Cunningham Ltd., Manure and Cake Manufacturers, Leith. Appointed Agricultural Analyst to Colombo Commercial Co., Ltd., Ceylon.

James Walker. John Foggie.
John S. Lumsden. James Hendrick.
F. R. Japp.

Kenyon, Joseph,

6, Cheltenham Street, Blackburn.

Demonstrator in the Chemical Department of the Blackburn Technical School. B.Sc. (Lond.) 2nd class honours in chemistry. Associate of the Institute of Chemistry. Joint Author of the following papers which have appeared in the Journal of the Society. 'Contributions to the Chemistry of Oxygen Compounds." Part I. *Trans.*, 1906, 262. Part II. *Trans.*, 1907, 896. "The Resolution of Sec. Octyl Alcohol," *Trans.*, 1907, 2058.

Robert H. Pickard. W. H. Duckworth.
Joseph Yates. W. E. Bickerdike.
T. Martin Lowry.

Linch, Frank William,

9, Gladstone Avenue, Manor Park, London, E.

Lecturer and Demonstrator on Chemistry. Three years Student at City and Guilds Tech. Coll., Finsbury. Last three years Lecturer and Demonstrator at Northern Polytechnic Institute, London, N. Associate of the Institute of Chemistry. Int. B.Sc.

R. Meldola. W. H. Mills.
John Castell-Evans. John Spiller.
W. H. Glover.

Lindley, Arthur Stanley,

Prince Building, Medows Street, Bombay.

Analytical Chemist. Five years Assistant Analyst to Mr. Edward Riley, F.I.C., F.C.S., &c. Twenty-one months Chemist at Lord St. Oswald's Ironstone Mines, Frodingham, Lincolnshire. Fifteen months Chemist to The Goa Mining Co., Portuguese India. At present in charge of Messrs. Edward Riley & Co.'s Laboratory and Assay Offices, Bombay, India.

Edward Riley. A. W. Comber.
Herbert H. Dains. *Claude S. Fawcitt.*
C. D. Morewood.

MacGregor, Gregor,

Giffen Park, Dysart, Fife.

Headmaster, Viewforth Higher Grade School, Dysart. Teacher of Chemistry in same, also Headmaster Science and Art School, Viewforth, Dysart. M.A. (Glasgow). Chemistry, with Chemistry Laboratory experience. B.Sc. (Glasgow). Applied Science (Agricultural Chemistry, &c.). Six months Chem. Laboratory, West of Scotland. Agricultural College, First Prizeman (Chemical Analyses of Manures, Foods, &c.). Two years under A. Wilson, F.I.C., Stirling. Science Master and Analytical Chemist. Senior Chemistry Master, Wigan Grammar School, January, 1904, to July, 1908. Taught Chemistry, with Quantitative Chemical Analysis.

Ernest Brooks Naylor. G. Crewe Chambres.
Thomas Henry Byrom. Alfred H. Scholefield.
W. H. Leek.

Menzies, Frederick Martin Kay,

79, Davies Street, Berkeley Square, W.

Assistant Medical Officer of Health, and Demonstrator Public Health Laboratory, University College, London. M.D., F.R.C.P. (Edin.), D.P.H. (conjoint London).

H. R. Kenwood. N. T. M. Wilsmore.
Edward C. Cyril Baly. William Ramsay.
J. N. Collie.

Miles, William Herbert,

3, Liversidge Road, Higher Tranmere, Birkenhead.

Analytical Chemist. Student for three years under Dr. George Tate, F.I.C. Analytical Chemist, Liverpool. Assistant in the employ of Messrs. Evans Sons, Lescher and Webb, Limited, Liverpool, three

and a half years. Analyst to the Mersey Oil and Cake Mills Co., Limited, Liverpool, two years (present occupation).

George Tate. F. Robertson Dodd.
Alfred Smetham. John Hanley.
Thomas J. Roberts.

Millar, Charles James,
c/o Messrs. Turner, Morrison, and Co., Calcutta, and 23, James Street, Greenhead, Glasgow.

Analytical Chemist. Attended classes and have certs. for full course of study in Glasgow and West of Scotland Technical College; certs., including 1st prize (1st class), Organic Chemistry. Also certs. in Technical Chemistry, including oils and fats, coal analysis, and dyeing and bleaching. Personal recommendation from Prof. Henderson of above College. Five years with Messrs. T. Henshelwood and Co., Glasgow Oil, Paint, and Colour Works. Two years with Messrs. British Dyewood and Chemical Co. as Chemist, and at present chemist in Calcutta with Messrs. Turner, Morrison and Co.

Wm. B. Jackson. G. G. Henderson.
Thomas Gray. William S. Denham.
A. B. Steven.

Minett, Edward Pigott,
Guy's Hospital, S.E.

Doctor of Medicine, and Member Royal College of Surgeons, Licentiate Royal College of Physicians. Pharmaceutical Chemist (highest record marks). Student and Assistant Chemical Laboratory of Dr. Muter. Assistant Messrs. John Bell and Co., Oxford Street, W. Assistant Bacteriological and Public Health Laboratory, Guy's Hospital, S.E.

Thos. Stevenson. J. H. Ryffel.
John Wade. Walter C. Ball.
H. Finnemore.

Morgan, Howard Houlston, B.Sc., A.R.C.S.,
Technical College, Auckland, New Zealand.

Science and Mathematical Master. Experience of Chemistry as Student and Teacher. Bachelor of Science (Lond.), Honours in Chemistry. Associate of the Royal College of Science (Three Years Internal Student National Scholar in Chemistry).

H. E. Hadley. G. T. Morgan.
William A. Tilden. G. S. Newth.
M. O. Forster. James C. Philip.

Norman, Cyril Lawrence,

36, Halesworth Road, Lewisham, S.E.

Student of Chemistry. Certificated Student of City and Guilds Technical College, Finsbury. Matriculated Student of London University.

R. Meldola. F. Stanley Benton.
John Castell-Evans. Chas. R. Darling.
Edward W. Bealey. Leslie H. Berry.

Normand, Alexander Robert,

8, Hillside Street, Edinburgh.

Lecturer on Chemistry, Wilson College, Bombay. M.A., B.Sc. (Edinburgh). Lecturer on Chemistry, Wilson College, from 1902.

Alex. Crum Brown. J. P. Longstaff.
Leonard Dobbin. John E. Mackenzie.
Hugh Marshall.

Pearson, George Edward,

Snow Hill Buildings, London, E.C.

General Manager, Burroughs Wellcome & Co., Manufacturing Chemists, London, E.C.

Henry E. Armstrong. Frederick B. Power.
Edward C. Cyril Baly. H. A. D. Jowett.
W. B. Tuck. *J. N. Collie.*

Pearson, John William,

Buxton College, Derbyshire.

Science Master. Second Class Honours, Cambridge Natural Science Tripos, 1904. Six months' work in a London Analytical Laboratory. Four years Chemistry teaching. A desire to keep abreast of the times in Chemical Science.

Edward D. Walrond. Charles T. Heycock.
F. H. Neville. Robert Wright.
E. H. Farr.

Perry, Frank,

63, Tunnel Street, Coseley, near Bilston, Staffs.

Analytical and Research Chemist. Four (4) years at Finsbury Technical College. General Commercial Analysis one year. Assistant Chemist to Messrs. Howards & Sons, Ltd., of Stratford, for two years. Research Chemist to Sherard, Cowper-Coles & Co., and "Metalloids," Ltd., Tipton, for two years. Published joint

paper with Bernard Howard, Esq., before the Society of Chemical Industry, 5th December, 1905.

R. Meldola. Edward W. Bealey.
John Castell-Evans. W. Hansen Rawles.
Leslie H. Berry. F. Henry Streatfeild.

Power, George O'Brien,

Fatehpur, U. P. of Agra and Oudh, India.

Assistant Opium Agent. I have studied chemistry at the Civil Engineering College, Sibpur (Calcutta), and wish to keep myself in touch with current literature, and, more particularly, with modern developments of the chemistry of alkaloids.

Paul Brühl. William Tate.
E. R. Watson. *P. C. Ray.*

David Hooper.

Rennie, Alexander,

Johannesburg, Transvaal.

Chemist, Druggist, and Pharmacist (Transvaal). Ex-President of the Pharmaceutical Society of the Transvaal, Member of the Pharmaceutical Society of Great Britain, Queen's Prizeman and Holder of three First-Class Certificates in Chemistry, Science, and Art Department, London, &c.

Walter C. C. Pakes. Thos. William Dukes.
B. Owen Jones. *J. A. Wilkinson.*

Peter MacEwan.

Rhead, Ezra Lobb,

Stonycroft, Polygon Avenue, Levenshulme.

Lecturer on Metallurgy, Municipal School of Technology, Manchester, and author of (I) "Metallurgy, an Elementary Text-book"; (II) Assaying and Metallurgical Analysis" (Rhead and Seaton); (III) "The Art and Practice of Ironfounding" [In the Press]; (IV) "Papers Dealing with the Introduction and Removal of Sulphur from Iron; Loss in Estimation; and on other Metallurgical Subjects"; (V) "The Estimation of Copper by Titanous Chloride."

William J. Pope. Jas. Grant.
W. H. Perkin, jun. R. L. Taylor.

S. J. Peachey.

Roach, William Frothingham,

Royal Mersey Yacht Club, Rock Ferry, Cheshire.

Medical Officer, Colonial W. African Service. Doctor of Medicine, and Master of Surgery, University Bishop's College, Montreal; Licentiate Apothecaries' Hall, Dublin; Pharm. Chemist Montreal

College of Pharmacy; Member Ph. Assn. Prov. of Quebec; 3 years student under Dr. Harrington McGill doing analysis.

David Sommerville. Rhys P. Charles.
T. H. Byrom. J. T. Ainslie Walker.
Samuel Rideal.

Salamon, Maurice Salamon,
64, Oxford Gardens, N. Kensington.

Student. Intermediate Science, London, 1906. Student at University College for 4 years.

J. Norman Collie. N. T. M. Wilsmore.
William Ramsay. Edward C. Cyril Baly.
R. H. Aders Plimmer.

Saunderson, William,
The Armidale School, Armidale, New South Wales.

Science Master at the above school. Bachelor of Science of Durham University; Science Master at Langport Grammar School, Somerset, Leathersellers' Company Colfe Grammar School, extending over a period of seven years.

P. Phillips Bedson. F. C. Garrett.
J. A. Smythe. *S. Hoare Collins.*
C. Harold Oxland.

Sommerfeldt, Dr. Ernst,
4, Pollock Street, Calcutta.

Universitäts-Professor. Dr. Ph. in Chemistry, Phys., and Miner. at Göttingen, Germany). Co-editor of the periodical *Zeitschrift f. wissenschaftl. Mikroscopie*, Leipzig.

Edward C. Cyril Baly. N. T. M. Wilsmore.
W. H. Pearson. J. W. Swan.
J. E. Stead.

Tate, Francis George Henry,
Kilmersdon, Homecroft Road, Sydenham, S.E.

Assistant Analyst in the Customs Branch of the Government Laboratory, Two years' training in Chemistry at the Royal College of Science, 1900–1902. Worked as an Assistant Analyst in the Customs Branch of the Government Laboratory since 1902.

T. E. Thorpe. William A. Tilden.
J. Connah. G. T. Morgan.
Thos. J. Cheater. M. O. Forster.

Thomas, Frank Moreton,

290 Rotton Park Road, Edgbaston, Birmingham.

Stores Superintendent, c/o Messrs. Belliss and Morcom, Ltd. Mechanical and Electrical Engineers, Birmingham. Author of the following papers, read before the Metallurgical Society and the British Foundrymen's Association at Birmingham, and printed in the journals named: "Pig-iron in its Commercial Aspects" (*Iron and Coal Trades Review*); "Properties of Steel" (*Mechanical Engineer*); "Selection and Testing of Foundry irons" (*Castings*, and *Mechanical Engineer*). Contributor of a series of technical articles to *Birmingham Technical School Magazine*. Member of Iron and Steel Institute. Member of Council, Metallurgical Society, Birmingham. Honours Certificate City and Guilds of London Institute, "Iron and Steel Manufacture," etc.

Thomas Turner. Douglas Twiss.
Henry Silvester. A. E. Bond.
Lionel M. Jones.

Walton, Sidney Gilbert,

"Kensington," Northwood Road, Northwood, Lane Cove River, N.S.W.

Assistant Analyst, Government Laboratory, Department of Public Health, Sydney. For five years I was Junior Assistant to the late Dr. Helms, Analyst of Sydney, after which I studied Chemistry for three years at the University of Sydney, taking a special course in Food and Drug Analysis, and was later appointed Junior Demonstrator in Chemistry, which position I resigned for the purpose of taking up my present duties. During the last two years I have been Assistant Examiner at the Annual Examinations in Chemistry at the University of Sydney. A paper on the Composition of Chocolate Shale and of Tufaceous Sandstone from the Narrabeen Series was contributed by me, and read by Prof. Liversidge, M.A., F.R.S., &c., before the Royal Society, on December 5th, 1906.

William M. Hamlet. Henry G. Smith.
W. M. Doherty. F. B. Guthrie.
J. A. Schofield.

Watt, Robert Dickie,

Pretoria, Transvaal (P. O. Box 434).

Acting Chief Chemist to the Transvaal Department of Agriculture. M.A. degree (Glasgow) 1903. B.Sc. (in Agric.) degree (Glasgow) 1905. 1905—07, Carnegie Research Scholar. Worked at Rothamsted, Herts. Publication, "On the Gas Evolved on Churning," in Journal

Agric. Science, Vol. II. No. I. 1907. Assistant Chemist, Transvaal Department of Agriculture, 1908. Acting Chief, ditto.

A. D. Hall. E. J. Russell.
N. H. J. Miller. *J. Augustus Voelcker.*

Bernard Dyer.

Weighell, Arthur,

Top Floor, Prince Building, Medows Street, Fort, Bombay.

Analytical Chemist. Four years Student at Rutherford College, Newcastle-on-Tyne. Five years with Messrs. J. & H. S. Pattinson, Newcastle-on-Tyne, as Assistant. Eight months with Messrs. Edwd. Riley & Co., Bombay, as Assistant. At present in partnership with Mr. A. S. Lindley, Bombay, as Analyst.

Claude S. Fawcitt. J. T. Dunn.
John Pattinson. *A. W. Comber.*

Edwd. Riley.

Williams, Frederick,

Bute Villa, Aberdare, S. Wales.

Chemistry Master at the Secondary School, Ferndale, S. Wales. B.A. (Oxon.). Honours in Chemistry, Final Honour School, 1907.

Andrea Angel. J. E. Marsh.
H. B. Baker. W. W. Fisher.

John Watts.

Winterson, William George,

89, Salisbury Road, Barnet.

Chemical Assistant, under Dr. McGowan, to the Royal Commission on Sewage Disposal. B.Sc. (Lond.) Chem. Hons., 1905. Joint author with Mr. E. S. Kitchen, of paper, "Malacone, a Silicate of Zirconium containing Argon and Helium," *Trans., Chem. Soc.*, 1906, vol. 89. Engaged, since June, 1906, under Dr. McGowan, in the Chemical work of the Royal Commission on Sewage Disposal, and in other analytical work.

George McGowan. N. T. M. Wilsmore.
William Ramsay. J. Norman Collie.

R. W. Gray.

Wootton, William Ord,

159 Maidstone Rd., Rochester.

Assistant Demonstrator in Chemistry Royal College of Science, London. B.Sc., (Lond.). Honours in Chemistry. A.R.C.Sc. (First Class). Part author with Dr. G. T. Morgan, F.I.C., of papers published in the Journal of the Society 1905—1907. Author of a paper on

"Aromatic Amides and Imides of Camphoric Acid" (*Trans. Chem. Soc.*, 1907, vol. 92).

William A. Tilden. G. T. Morgan.
M. O. Forster. James C. Philip.
Chapman Jones.

Worley, Frederick Palliser,

Mansfield House, Clifton Gardens, Maida Hill, London, W.

Research Student of Chemistry (City and Guilds of London Institute, Central Technical College). Graduate of New Zealand University, M.A., M.Sc. First Class Honours in Chemistry. Paper on "Bromide in Solutions of KBr·Ag," published in the *Journal of the Chemical Society*, 1905 (pp. 1107—1123).

Henry E. Armstrong. Walter H. Glover.
William Robertson. John Vargas Eyre.
Edward Wheeler.

Wright, Allister MacLean,

Christchurch, New Zealand (P.O. Box 617).

Analytical Chemist (The Christchurch Meat Co., Limited). Five years Analytical Chemist to the Christchurch Meat Co. Author of "The Meat Extracts of New Zealand"; "Spontanous Combustion in Wool"; "Analysis of some New Zealand Coals" (*Journal Soc. Chem. Ind.*); "New Zealand Boned Beef" (*Chem. News*); two papers on "Nitrogen-Fixing Bacteria"; "New Zealand Coals"; "New Zealand Meat Products" (*Trans. N.Z. Inst.*).

George Gray. Geo. M. Thomson.
Robert English. B. C. Aston.
Geo. Bagley.

The following Certificates have been authorised by the Council under Bye-law I (3):

Allen, Thomas Boles,

Medical Faculty, McGill University, Montreal.

Demonstrator of Chemistry. B.A. in Chemistry and Mineralogy, Univ. of Toronto, 1901. M.A., 1907. Assistant in Chemistry Dept. of Chem. Univ. of Toronto, 1906—1907. Demonstrator in Chemistry and Physics, Dept. of Chemistry, Medical Faculty, McGill Univ.,

Montreal, 1907. Joint author with Prof. W. R. Lang of Paper on "An Improved Form of Apparatus for Estimation of Sulphates and Salts of Barium," *Trans.*, Chem. Soc., 1907. Vol. 91.

W. R. Lang. J. Wallace Walker.
W. Lash Miller. Nevil Norton Evans.

Ba, Maung,

Rangoon College, Rangoon.

Assistant to Science Lecturer, Rangoon College. B.A., Calcutta, 1899. Assistant to Science Lecturer, Rangoon College, since January, 1901. Acts as Assistant Lecturer and Demonstrator in the Laboratory.

M. Hunter. *Thein Kin.*

Bhunsri, Prince Mom Chow,

23, Ashburn Place, London, S.W., or Saranrome Palace, Bangkok, Siam.

Future estate agent to His Royal Highness the Crown Prince of Siam. Associate of the Royal Agricultural College (by examination). Being interested in Agricultural Chemistry.

Edward Kinch. *J. Augustus Voelcker.*
W. W. Cobb.

Krishnayya, H. V.,

Mallesvaram, Bangalore, Mysore, India.

Assistant Chemist, Government Chemical Laboratory. B.A. (Madras). Engaged for the last twelve years in the analysis of rocks and minerals in the Chemical Laboratory at Bangalore.

A. L. F. Lehmann. Morris W. Travers.
Claude S. Fawcitt.

San, Maung U.,

Rangoon.

Assistant to the Chemical Examiner and Bacteriologist to the Government of Burma. Assistant in the Laboratory of the Chemical Examiner, Burma, since June, 1904. At first in charge of the examination of oils, and more recently Chief Assistant on the Medico-legal side of the Laboratory.

M. Hunter. Thein Kin.

Shilstone, Herbert M.,

No 410, South Front Street, New Orleans, La.

Analytical Chemist. Bachelor of Science degree. Nine years'

practical experience as Analytical Chemist. Recent Assistant Prof. Chemistry at N.O. College of Pharmacy.

John R. Bovell.

Watt, The Rev. John,

Scottish Churches College, Calcutta.

Professor of Chemistry. M.A., Aberdeen, 1884. A Teacher of Science of several years' standing.

P. C. Rây. J. A. Cunningham.

R. CLAY AND SONS, LTD., BREAD ST. HILL, E.C., AND BUNGAY, SUFFOLK.

Issued 11/12/08

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 24 **No. 348.**

Thursday, December 3rd, 1908, at 8.30 p.m., Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs.:

Herbert Edwin Cocksedge, B.A., 5, Romola Road, Herne Hill, S.E.
Frederick Percy Dunn, B.Sc., Haresfield, Chorley Wood.
Frederic Ferraboschi, B.A., Clare College, Cambridge.
Walter Norman Haworth, M.Sc., Dacca House, Chorley.
Eric Hayward, c/o W. R. Criper, Esq., Konnagar House, Konnagar, Nr. Calcutta.
Robert Ernest Jackson, York Villa, Shepherd's Lane, Dartford.
John Hugh Jeffery, 10, Daysbrook Road, Streatham Hill, S.W.
Joseph Allen Pickard, B.Sc., 3, West Kensington Terrace, W.
David Segaller, 69, Dover Road, Wanstead Park, E.
Reginald Wells Varley, 12, Mill Hill Road, Derby.

A ballot for the election of Fellows was held, and the following were declared duly elected:

Noel Charles Akers.
Thomas Boles Allen, M.A.
Thomas Aubertin, B.A.
Maung Ba, B.A.
Thomas James Baker, D.Sc.
Maurice Barrett.
Prince Mom Chow Bhunsri.
Robert Bickerstaffe.
William Colet Birch, B.A.
William Sudderick Brakes.
Leonard Clement, B.A.
Robert Charles Cowley.
Hugh Cecil Duckworth.
Horace Barratt Dunnicliff, B.A., B.Sc.
Reginald Freeman Easton.

Charles Everitt, M.A.
Henry Fairburn.
Arthur Frank Girvan, B.Sc.
Henry Hamilton Green.
John Griffin, B.A.
John Henry Albert Hebron, B.Sc.
Edward Hinks, B.Sc.
Joseph Albert Hughes.
Thomas Ernest Hull.
James Colquhoun Irvine, D.Sc., Ph.D.
Grove Johnson.
Patrick Anderson Keiller, B.Sc.
Joseph Kenyon, B.Sc.
H. V. Krishnayya, B.A.
Frank William Linch.
Arthur Stanley Lindley.
Gregor MacGregor, M.A., B.Sc.
Frederick Martin Kay Menzies, M.D., F.R.C.P.
William Herbert Miles.
Charles James Millar.
Edward Pigott Minett, M.D., M.R.C.S., L.R.C.P.
Howard Houlston Morgan, B.Sc.
Cyril Lawrence Norman.
Alexander Robert Normand, M.A., B.Sc.
George Edward Pearson.
John William Pearson, B.A.
Frank Perry.
George O'Brien Power.
Alexander Rennie.
Ezra Lobb Rhead.
William Frothingham Roach, M.D.
Maurice Salomon Salomon.
Maung U. San.
William Saunderson, B.Sc.
Herbert M. Shilstone, B.Sc.
Ernst Sommerfeldt, Ph.D.
Francis George Henry Tate.
Frank Moreton Thomas.
Sidney Gilbert Walton.
John Watt, M.A.
Robert Dickie Watt, M.A., B.Sc.
Arthur Weighell.
Frederick Williams, B.A.
William George Winterson, B.Sc.
William Ord Wootton, B.Sc.
Frederick Palliser Worley, M.A., M.Sc.
Allister McLean Wright.

Of the following papers, those marked * were read :

***251. "Double salts of potassium iodide with mercuric iodide and dimercuriodocamphor in organic solvents." By James Ernest Marsh and Robert de Jersey Fleming Struthers.**

When an aqueous solution of the compound K_2HgI_4 is shaken with ether, ethyl formate, or some other organic solvents, the salt, $KHgI_3$, is extracted; it separates from its solution in ethyl formate as a heavy oil. In no case was the original salt, K_2HgI_4, dissolved. With camphor, the *double* salt, $KHgI_3,4C_{10}H_{16}O$, was obtained from dilute alcohol in light yellow, gritty crystals melting at 65°.

Potassium iodide and dimercuriodocamphor, $C_{10}H_{14}OHg_2I_2$, also form a *double* salt readily soluble in acetone or alcohol, although the two constituents are separately very sparingly soluble.

***252. "The action of mercuric iodide on ketones in alkaline solution." By James Ernest Marsh and Robert de Jersey Fleming Struthers.**

Acetone reacts with mercuric iodide in cold aqueous potassium hydroxide according to the equation :

$$C_3H_6O + 8HgI_2 + 6KHO = C_3OHg_5I_4 + 3K_2HgI_4 + 6H_2O.$$

Diethyl ketone reacts mainly according to the following equation:

$$(C_2H_5)_2CO + 6HgI_2 + 4KHO = (CH_3 \cdot CHg_2I_2)_2CO + 2K_2HgI_4 + 4H_2O.$$

Acetophenone reacts as follows:

$$C_6H_5 \cdot CO \cdot CH_3 + 6HgI_2 + 4KHO = HgI,C_6H_5 \cdot CO \cdot CHg_3I_3 + 2K_2HgI_4 + 4H_2O.$$

The ketone mercury compounds form yellow precipitates. Both the yield and the composition of the precipitates agree with the equations given. In the case of acetone and diethyl ketone, standard alkali was used, and the amount converted into potassium iodide was determined. This amount also agrees with the above equations. The reaction thus affords a quantitative method for estimating the amount of ketones, either by weighing the precipitate formed, or by determining volumetrically the amount of alkali neutralised in the reaction.

*253. "**The condensation of camphor with mercuric iodide.**" **By James Ernest Marsh and Robert de Jersey Fleming Struthers.**

The following series of mercury camphor derivatives has been obtained:

(*A*) $(C_{10}H_{15}OHg)_2O$, and its salts; (*B*) $C_{10}H_{14}OHg_2I_2$; (*C*) $(C_{10}H_{14}O)_2Hg_3O$; (*D*) $(C_{10}H_{14}O)_3Hg_4I_2$; (*E*) $(C_{10}H_{14}O)_4Hg_5I_2$; (*F*) $(C_{10}H_{14}O)_5Hg_6I_2$.

Of these compounds, *B*, *D*, *E*, and *F* are formed directly by the action of mercuric iodide on camphor in the presence of alkali. *B* is formed by the action of potassium ethoxide in alcoholic solution on camphor and mercuric iodide in the cold.

D is formed in a hot aqueous solution of potassium hydroxide containing excess of potassium iodide.

E is formed in a similar way with just sufficient potassium iodide to retain the mercuric iodide in solution.

F is formed when there is a defect of potassium iodide.

B is formed from *D* or *E* by the prolonged action of hot potassium hydroxide until all the iodine is removed.

Glacial acetic acid converts *D* into the *compound*, $C_{10}H_{14}OHg_2I_2$, which is insoluble, and the acetate of mercury camphor, which dissolves. From the latter, the base *A* is separated by the action of sodium hydroxide. The base forms salts, of which the *benzoate*, *sulphate*, *chloride*, *bromide*, and *iodide* have been prepared.

Discussion.

Dr. M. O. Forster inquired whether definite products had been obtained by the dry distillation of these derivatives of camphor, some of which might be expected to yield dehydrocamphor; also whether any therapeutic value had been observed in connexion with them.

Mr. Marsh replied that the compound $C_{10}H_{14}OHg_2I_2$ could be sublimed without decomposition, and that the other compounds decomposed, but the products formed had not been examined.

The material used in the experiments was the ordinary dextrorotatory camphor; the therapeutic and physiological action of the compounds had not yet been investigated.

***254. "The relation between absorption spectra and chemical constitution. Part XIII. Some pyrones and allied compounds." By Edward Charles Cyril Baly, John Norman Collie, and Herbert Edmeston Watson.**

The absorption spectra of dimethylpyrone, chelidonic acid, xanthochelidonate, ethyl diacetylacetone, and several other substances have been examined in considerable detail. In many cases the spectra vary with the solvent used, and consequently it seems probable that these compounds can exist in more than one form. Diacetylacetone in particular may be either an open-chain compound or one with a ring formation.

The pyrones and their simpler derivatives appear to contain an oxygen bridge, the atom of oxygen in the ring being quadrivalent. This bridge is broken by the addition of a sufficient quantity of alkali, intermediate compounds being sometimes formed.

***255. "Organic derivatives of arsenic. Part I. Dicamphorylarsinic acid." By Gilbert T. Morgan and Frances M. G. Micklethwait.**

Dicamphorylarsinic acid, $HO{\cdot}OAs(C_{10}H_{15}O)_2$, colourless, prismatic crystals, m. p. 266°, $[\alpha]_D$ 186·6°, is precipitated by acids from an alkaline extract of the product of the interaction of arsenious chloride and sodium camphor in toluene. Its *silver* salt, $AgO{\cdot}OAs(C_{10}H_{15}O)_2$, is a white, sparingly soluble substance, whereas its alkali salts dissolve readily either in water or alcohol. The acid is hydrolysed into camphor (2 mols.) and alkali arsenate (1 mol.), but only when its solution in aqueous caustic alkalis is evaporated almost to dryness.

When treated with phosphorus pentachloride, the acid gives rise to a *chloride*, from which the *anilide* may be obtained.

The authors are engaged in a study of the reactions occurring between the chlorides of the non-metals and organic compounds containing the characteristic group $CH_2 \cdot CO$.

Discussion.

Dr. Lowry said he had gathered from the title that the compounds to be described were derivatives of camphoric acid. The use of the term "camphoryl" in this sense had been rendered inevitable by the analogy of "acetyl," "benzoyl," "carbonyl," etc., and had been so generally recognised that no alternative name had hitherto been suggested. The use of the same term for the camphor radicle $C_{10}H_{15}O$ was bound to lead to confusion, and it was very desirable that some distinguishing name should be adopted for this group. Camphor derivatives had usually been named by means of prefixes, but the case of "camphocarboxylic acid" suggested an alternative usage: could not the arsenic compound be described by an analogous name as "dicamphoarsenic acid"?

Dr. M. O. Forster defended the use of the expression "camphoryl" for the complex $C_{10}H_{15}O$, and invited Dr. Lowry to formulate "dicamphorylarsinic acid" on his assumption that camphoryl should stand for the radicle of camphoric acid.

In reply to Dr. Pyman, Dr. Morgan said that they had not hitherto obtained the corresponding arsonic acid from the products of this condensation. With reference to the question of nomenclature raised by Dr. Lowry, it seemed to the authors that the prefix "camphoryl" was a suitable one to use for this acid, in which opinion they had the support of other investigators of camphor derivatives.

*256. "Tellurium dicyanide." By Herbert Edwin Cocksedge.

When tellurium tetrabromide and silver cyanide are heated together for some days in boiling benzene, tellurium dicyanide is formed.

On extracting the residual silver salts with ether, and evaporating the ether at the ordinary temperature, white crystals of the composition $2Te(CN)_2,(C_2H_5)_2O$ are obtained. By heating these and subliming the product in a vacuum, the pure *dicyanide*, $Te(CN)_2$, results in the form of white crystals.

The compound is partly decomposed by heat, giving cyanogen and tellurium. It is at once hydrolysed by water, with precipitation of black flocks of tellurium.

***257. "Boron thiocyanate." Herbert Edwin Cocksedge.**

Boron thiocyanate, $B(SCN)_3$, is prepared by the action of boron bromide on silver thiocyanate in cold benzene solution. On evaporation of the solvent at the ordinary temperature, colourless crystals remain.

The compound resembles the corresponding thiocyanates of phosphorus and silicon in general reactions, but decomposes readily on heating. The action of aniline on the compound in benzene solution points to the thiocyanate constitution.

***258. "The viscosity of fuming sulphuric acid." By Albert Ernest Dunstan and Robert William Wilson.**

The authors have investigated the viscosity-concentration curve afforded by various mixtures of sulphuric acid and sulphur trioxide. They find a maximum point at the concentration corresponding with H_2SO_4,SO_3.

Discussion.

Dr. Senter said that the maxima in the curves for binary mixtures obtained by plotting viscosity against composition were usually somewhat difficult to interpret. Both sulphuric acid and water appeared to exist as very complex molecules in the pure state, and it was probable that both of them were in a simpler molecular condition when mixed. He wished to ask Mr. Dunstan how, in his opinion, the viscosity curve would be affected by a progressive simplification of the molecules of the components on dilution. If it was assumed that, owing to the increased surface of the particles, the effect of this simplification was to increase the viscosity, the maximum in certain binary mixtures of associated liquids (for example, alcohol and water) could be accounted for without assuming that the components enter into chemical combination. On the other hand, independent evidence pointed to the existence of chemical compounds in mixtures of sulphuric acid and water, and the latter system was therefore very complicated.

Mr. Dunstan, in reply to the President, agreed as to the advisability of determining the molecular surface energy of the mixture, the composition of which approximated to H_2SO_4,SO_3; in answer to Dr. Senter, he said that there were two explanations to the maximum points in viscosity-concentration curves; Jones and Veazey (*Amer. Chem. J.*, 1907, **37**, 405) have asserted that such maxima are due to dissociation, that is, by the proportionally larger frictional surfaces of smaller molecular masses, but he himself contended that in the first place the maxima

correspond with aggregates of simpler molecular composition, that such aggregates have actually been isolated, and that heat effects and many other physical properties attain their maxima at the same points. The argument as to larger frictional surfaces only held good if it were definitely known that the aggregates are regular in shape and smooth in surface.

Moreover, since associated substances were proportionately more viscous than non-associated compounds, he considered that the action of the sulphuric acid on the water (and vice versa) was (1) simplification of the homogeneous aggregates, and then (2) association of these products.

259. "The decomposition of carbon dioxide by the silent electric discharge." By Alfred Holt, jun.

Carbon dioxide, which had been carefully dried by phosphoric oxide, was found to be decomposed to an amount which increased as the pressure of the gas diminished. About 48 per cent. decomposition was obtained under 30 mm. pressure, and about 3 per cent. decomposition under 700 mm. pressure.

The amount of decomposition was found to vary with the degree of dryness of the gas, the intensity of the discharge, and the form of ozoniser employed, but in all cases diminished pressure gave greater decomposition.

Moist carbon dioxide was found to decompose to a larger extent as the pressure of the gas increased, ranging from 3 per cent. decomposition under 50 mm. pressure to about 14 per cent. under 700 mm. pressure. The weaker the discharge the less gas was decomposed at all pressures.

Comparison of these results with those obtained when moist and dry carbon dioxide is decomposed by ultra-violet light, or induction sparks, leads to the conclusion that the silent discharge at low pressures acts chemically, mainly like ultra-violet light, whilst as the pressure of the gas increases, it behaves more and more as though it consisted of actual sparks.

260. "Note on oxalyl chloride."
By Humphrey Owen Jones and Hubert Sanderson Tasker.

The authors' investigations on the properties and reactions of oxalyl chloride had been in progress some months when a paper on the same subject was published by Staudinger (*Ber.*, 1908, **41**, 3558). It was found, in agreement with Staudinger, that the yield of oxalyl chloride

obtained by Fauconnier's method, namely, by the action of phosphorus pentachloride on ethyl oxalate, is very poor, but the yield can be enormously increased by carrying out the reaction at 160° under pressure.

It was found impossible to free the oxalyl chloride entirely from phosphorus compounds by distillation, as the process is rendered more difficult by the presence of *as*-dichloroethane among the products. The amount of phosphorus trichloride formed is small, and the chief product is phosphoryl chloride; ethyl chloro-oxalate and ethyl trichloroacetate are formed in large quantities.

The major portion of the oxalyl chloride distils at about 70°, and then contains about 3 per cent. of phosphoryl chloride. Oxalyl chloride reacts vigorously with water, and yields some oxalic acid, together with carbon monoxide and carbon dioxide, whereas Staudinger states that oxalic acid is only obtained when the vapours react.

Oxalyl chloride reacts vigorously with primary and secondary amines to produce substituted oxamides, whereas with tertiary amines it forms additive products. The *additive* compound with pyridine, $C_2O_2Cl_2,2C_5H_5N$, is a white solid, which reacts with water to give pyridine hydrochloride with carbon monoxide and dioxide, and no oxalic acid; it reacts with primary or secondary bases to give pyridine hydrochloride and substituted oxanilides. This is a better method of preparing these substances than by using the chloride direct. The compounds formed with tertiary amines resemble closely the corresponding compounds obtained from carbonyl chloride.

The authors are at present engaged in examining the reactions of oxalyl chloride on a number of substances, chiefly derivatives of organic metallic compounds.

261. "The densities of krypton and xenon." By Richard B. Moore.

The author has prepared pure xenon and krypton from the residues from 120 tons of liquid air. The density of xenon was found to be 65·35, and that of krypton 41·506, the atomic weights being, on the assumption that the gases are monatomic, 83·012 and 130·70 respectively (O = 16).

262. "The action of reducing agents on tannic and gallic acids." By Walter Myers Gardner and Herbert Henry Hodgson.

The object of the work was to devise a rapid and accurate method for the estimation of tannic and gallic acids, and it was thought that a quantitative yield of benzoic acid might be obtained on reduction.

Previous work on the action of reducing agents on these acids had been published by Böttinger (*Annalen*, 1890, **258**, 252) and Guignet (*Compt. rend.*, 1891, **113**, 200). The former obtained no reduction products, but using different conditions Guignet found that both tannic and gallic acids were converted into benzoic acids.

The authors have repeated Guignet's work, but obtained a very poor yield of benzoic acid. In the further work, the following were tried as reducing agents: zinc, sodium, magnesium, aluminium, sodium hyposulphite, and hydriodic acid; experiments being made in most cases under acid, alkaline, and neutral conditions. The general results were that tannic and gallic acids are little affected by neutral or acid reducing agents, but that they react readily in alkaline solution. In no case, however, was a quantitative yield of benzoic acid obtained, and this was shown to be due to the slow destruction of benzoic acid by alkaline reducing agents.

The original object of the investigation was therefore not attained, but several interesting observations were made.

263. "The action of iodine on phenols and a modified process for the estimation of tannic acid." By Walter Myers Gardner and Herbert Henry Hodgson.

In the preceding paper, the authors have shown that tannic acid in alkaline solution rapidly reacts with reducing agents, and, based on this observation, a quick and accurate method for the estimation of tannic acid has been developed. The process is carried out as follows: To an aqueous solution of tannic acid, standard iodine solution is added in excess. Aqueous sodium hydroxide is then added drop by drop until the colour due to the iodine disappears, after which concentrated hydrochloric acid is added in sufficient excess to precipitate the unabsorbed iodine, the amount of which is estimated by standard sodium thiosulphate. Two estimations are necessary in the case of commercial tannins. Firstly, that of the total iodine absorbed, and secondly, that of the iodine absorbed after removing the tannic acid from the solution by precipitation with gelatin; the difference giving the iodine absorbed by the tannic acid. Previous work by Messenger and Nortmann (*Ber.*, 1890, **23**, 2753), F. Musset (*Chem. News*, 1885, **51**, 42), and A. Moullade (*J. Pharm. Chim.*, 1905, **22**, 153) on somewhat similar lines has been repeated, and it has been further shown that the process is available for the estimation of many phenols, for example, phenol, catechol, quinol, salicylic acid, pyrogallic acid, and gallic acid, in addition to tannic acid. With these substances, the amount of iodine absorbed is in direct ratio to the number of hydroxyl groups present, one hydroxyl

group requiring one molecule of iodine; but with other phenols the reaction, although quantitative, is empirical. The presence of other groups, such as NO_2, NH_2, OMe, as well as the position of the hydroxyl groups in the benzene nucleus, was found to have a determining influence on the course of the reaction. Following Wijs's investigations on the action of Hübl's solution, the authors think that the active substance is the hypoiodate formed, but they are further investigating this assumption.

264. "Ester catalysis and a modification of the theory of acids." By Edward Fitzgerald and Arthur Lapworth.

The previous observations on esterification and ester hydrolysis in acetone already referred to (*Proc.*, 1908, **24**, 152, 153) have been confirmed and extended.

If it be assumed that hydrogen ions are responsible for acid catalysis in esterification and ester hydrolysis, the authors find it possible to explain the facts on one proposition only, namely, that the addition of water to a solution of an acid in acetone or alcohol greatly diminishes the number of hydrogen ions, the alternative theories—that the intermediate products are shared between the alcohol and water, or the view applied by Arrhenius to the hydrolysis of salts of weak bases—having proved inadequate.

It would then appear that the proportion of hydrogen ions in an aqueous solution of hydrogen chloride must be extremely small, and this makes it seem probable that they are not altogether indispensable to a satisfactory theory of acids.

The hydrated hydrogen ion or hydroxonium ion, $H_3\dot{O}$, often assumed to be the conducting positive ion in aqueous solution of acids, is, in this conception, inert as a catalyst, so that these suggestions are not only at variance with the Arrhenius-Ostwald view of connexion between conductivity and reactivity, but are essentially opposed to theories of hydrion catalysis in which the hydroxonium ion is regarded as catalytically active (compare Goldschmidt and Udby, *Zeitsch. physikal. Chem.*, 1907, **60**, 731).

In most physical measurements the hydrogen ions proper may be neglected, and the above theory virtually takes the form that the anticatalytic effect of water on catalysis by acids is due to the fact that water in the same sense as ammonia is a more powerful base than the solvent and, usually, the substance catalysed, and diminishes the available free acid by converting it into hydroxonium salt.

265. "An examination of the conception of hydrogen ions in catalysis, salt formation, and electrolytic conduction." By Arthur Lapworth.

Small quantities of water depress the catalytic effect of acids on the bromination of acetone and on the hydrazobenzene conversion in alcohol and other solvents in just the same way as in the case of esterification (Goldschmidt) and the decomposition of ethyl diazoacetate (Bredig). Water, to the extent of 0·5 per cent. in acetone itself, depresses the velocity with which it absorbs bromine under the influence of acids to considerably less than one-half of its original value.

Proceeding from the most generally accepted view that free hydrogen ions are responsible for catalysis by acids, a strict mathematical expression applying to the state of an acid in a medium is easily developed. By means of this it is not difficult to show that all the generalisation of Ostwald and Arrhenius applying to the variations of conductivity and catalytic activity with volume and the measured degree of dissociation will be as true when the medium consists of, or contains, a mixture of bases as when it is neutral; further, that all acids at infinite dilution in a given medium will exhibit the same equivalent catalytic activity. But this is mathematically true when the hydrogen ions in all cases are then made = 0.

In order to connect these conclusions with the basic properties of common oxygenated solvents, a simple indicator method has been devised. The phenomena observed with water on the indicator salt in alcohol, simulate closely the effects of water on acid catalysis. Using this process in several media, Mr. R. W. L. Clarke reports, as a first approximation to the real relative affinities of some weak bases: carbamide, 17; water, 1; ether, 0·12; ethyl alcohol, 0·06. The values are fairly concordant amongst themselves, and are of the expected order.

At the next Ordinary Meeting on **Thursday**, December **17th**, 1908, at **8.30** p.m., the following papers will be communicated:

"Silicon researches. Part XI. Silicotetrapyrrole." By J. E. Reynolds.

"Silicon researches. Part XII. Action of silicochloroform on potassium pyrrole." By J. E. Reynolds.

"Silicon researches. Part XIII. Silicon halides and pyridine, acetonitrile, etc." By J. E. Reynolds.

"The affinity values of tropine and its derivatives." By V. H. Veley.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 24 **No. 349.**

Thursday, December 17th, 1908, at 8.30 p.m., SIR WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

On the question of admitting women to the Fellowship of the Chemical Society, the PRESIDENT was desired by the Council to make the following statement:

As already announced, the recent ballot on this question showed that of those among the 2900 Fellows of the Society who voted, 1094 were in favour of, 642 opposed to, the admission of women to the full rights and privileges of Fellowship. Consequent on this difference of opinion three considerations presented themselves.

(1) In 1904 the opinion of Counsel was taken as to the eligibility of women for Fellowship under the existing Charter, and your Council was advised that married women are certainly excluded, whilst the position of unmarried women is extremely doubtful, and that it would not be wise to admit women to Fellowship without first applying for a Supplemental Charter. Such a course would involve the Society in considerable expense unless, as has been suggested, the cost were met in part by the petitioners; moreover, your Council was advised on a previous occasion when application for a Supplemental Charter with another object in view was under discussion, that in the opinion of Counsel it was "highly improbable that the Government department before whom the application must come would be disposed to listen to the application unless it represented the practically unanimous vote of the Fellows, and that any active

opposition by even a small minority would probably be fatal" (*Proceedings*, 1898, p. 38).

(2) Assuming, however, that a successful application for a Supplemental Charter were made, and a certificate of candidature on behalf of a woman were presented, the ballot, if reflecting the above-mentioned figures, would result in the rejection of the candidate, because at least three-fourths of those voting must be in favour.

(3) Your Council might accord to women the privilege of using the Library and attending the meetings, and allow them to purchase the publications of the Society at approximately cost price.

After mature deliberation your Council has decided by a considerable majority that it would remove some of the disabilities experienced by women chemists if the following resolution were adopted.

"That in the opinion of this Council it is desirable that, at any time, on recommendation by three Fellows of the Society, women be accepted as Subscribers to the Society. Such women Subscribers shall pay an annual fee of thirty shillings; they shall be admitted to all ordinary meetings of the Society; they shall have the same use of the Library as the Fellows, and they shall be supplied with the Proceedings, Transactions, and Annual Reports of the Society as these are issued."

This resolution has now been adopted.

It was further announced by the PRESIDENT that the Society was once more indebted to Sir Henry Roscoe for a valuable gift of books, comprising 636 volumes. The meeting endorsed with acclamation the vote of thanks already accorded Sir Henry by the Council.

The seventieth birthday of Professor Dr. G. Lunge will be celebrated on September 15th, 1909, and a local committee has undertaken to arrange a suitable commemoration of the occasion; the PRESIDENT stated that those Fellows who desire to show their sympathy with the festival are requested to communicate with Herrn Dr. E. Berl, Zürich IV, Sonneggstrasse 84.

Mr. M. Barrett was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs.:

George Henry Joseph Adlam, B.A., 86, Southmoor Road, Oxford.
Hubert Brunskill, 7, Friarage Gardens, Hartlepool.
John Wilberforce Green, 22, Alwyne Road, Wimbledon.
John Esson McGillvray, M.A., 15, Regent Street, Hartlepool.
William Norton Morley, B.Sc., 325, Brownhill Road, Catford, S.E.

Frederick Hubert Painter, B.Sc., Heatherbank, Alum Chine Road, Bournemouth.
Colston James Regan, 14, Penerley Road, Catford, S.E.
James Thomas Stevenson, 67, Surrey Street, Sheffield.

Of the following papers, those marked * were read :

***266. "Silicon researches. Part XI. Silicotetrapyrrole." By James Emerson Reynolds.**

Much of the work recorded in former papers of this series related to the action of silicon halides on aromatic compounds, including the amino-group, or its equivalent, as a side-chain. It was shown that well-defined, crystallised substances could be formed, such as $Si(NH{\cdot}C_6H_5)_4$, in which silicon was obtained for the first time wholly combined with nitrogen. In the course of the study of these substances, it became evident that the inquiry should be carried a stage or two farther, so as to include compounds in which nitrogen forms part of a ring, as in pyrrole and pyridine.

Silicon tetrachloride can be added to pure pyrrole with little effect, but when some light petroleum is poured in, complete mixture is effected and a brown condensation product, containing a small and variable proportion of silicon, separates out. This feeble action of the free base is in strong contrast with the violent interaction of aniline and the silicon compound.

It was found, however, that when potassium pyrrole, C_4H_4NK, was treated with silicon chloride at a low temperature, energetic action ensued, potassium chloride and a crystalline *substance*, in fine needles, which proved to have the composition $Si(NC_4H_4)_4$, being formed. This compound melts at 173° (corr.), but decomposes if heated to a materially higher temperature. Its molecular weight, as determined by the boiling-point method, agrees with the above formula. The substance differs materially from silicophenylamide more especially in the action of heat on it.

***267. "Silicon researches. Part XII. The action of silicochloroform on potassium pyrrole." By James Emerson Reynolds.**

As a synthesis of pyridine from pyrrole has been effected by the action of ordinary chloroform on potassium pyrrole, it seemed possible that silicochloroform might yield a silicopyridine, that is, a pyridine ring including SiH instead of one CH group.

Violent action occurs when silicochloroform is added to potassium

pyrrole, and the mass becomes dark brown or black, owing to the decomposition of a large proportion of the pyrrole, but nothing definite could be extracted from the residues of several such experiments save some of the tetrapyrrole compound described in Part XI. However, when the materials used were cooled to a very low temperature, the interaction was not so violent, and a small quantity of a dark green liquid was extracted, which did not boil at 210° under a pressure of 50 mm., and decomposed rapidly above that temperature. It proved to consist of $SiH(NC_4H_4)_3$ in a nearly pure condition. When cooled in liquid air, it became a deep bronze-green solid, but rapidly liquefied at the ordinary temperature. It is very easily decomposed in moist air.

Another compound was obtained during the preparation of the tripyrrole derivative; this is a liquid boiling at about 135°/50 mm., and has the composition $SiH(NC_4H_4)Cl_2$. It is easily decomposed by water, and fumes in the air. Neither this liquid nor the tripyrrole compound exhibits any characters of a silico-nitrogen-carbon ring, but they promise to prove useful in further attempts to form such a cyclic combination.

***268. "Silicon halides and pyridine, acetonitrile, etc. Part XIII." By James Emerson Reynolds.**

It was inferred from the experience obtained with pyrrole that organic substances, including nitrogen wholly combined with carbon, would react feebly, if at all, with silicon halides. A series of experiments has confirmed this view so far as applies to the compounds used, namely, pyridine, acetonitrile, propionitrile, and benzonitrile.

Pyridine gave with silicon tetrabromide the *additive* compound $SiBr_4,2C_5H_5N$, and the chloride yielded a similar substance, which latter was also obtained by Harden. Acetonitrile and propionitrile also gave *additive* compounds of the same order with silicon tetrabromide, and much less easily with the chloride, but benzonitrile did not appear to combine with either.

***269. "The affinity values of tropine and its derivatives." By Victor Herbert Veley.**

It was shown that tropine, the parent base of the atropine and cocaine alkaloids, has a considerably lower affinity value than piperidine, and it was concluded that the stronger piperidine residue is modified by being conjoined to the weaker pyrrolidine residue if the constitution of this base proposed by Willstätter is correct.

Ecgonine, or tropinecarboxylate, possesses all the properties of an amphoteric electrolyte; its nature is in all probability that of an inner anhydride or betaine.

Anhydroecgonine is a stronger base than ecgonine; the affinity value obtained was approximately equal to that of a benzenoid betaine.

Benzoylecgonine in dilute solution does not remain in combination with hydrochloric acid; its basic function is, therefore, of the order of caffeine.

Cocaine is a relatively strong base, although weaker than ammonia; the effect produced by the substitution of the carboxylic hydrogen by the methyl group is analogous to that previously observed in the case of glycine.

The affinity value of cocaine was found to be approximately $k_b = 2{\cdot}5\ 10^{-7}$, by determining the mass of sodium hydroxide, contained in a hydrolysed borax solution, which was required to upset the equilibrium between a certain mass of cocaine combined with hydrochloric acid as a dissolved salt.

The tropeines, atropine and homatropine, have affinity values greater than $k_b = 1\ 10^{-7}$; it appeared that when aqueous solutions of their hydrochlorides are heated for some time to their boiling point, no conversion of the lactonic group into the corresponding hydroxycarboxylic acid takes place.

***270. "Hydroaromatic ketones. Part I. Synthesis of trimethyl*cyclo*hexenone (*iso*phorone) and some homologues." By Arthur William Crossley and Charles Gilling.**

Further investigation of the trimethyl*cyclo*hexenone obtained by the interaction of ethyl malonate and chlorodimethyl*cyclo*hexenone (*Proc.*, 1908, **24**, 130) has proved it to be identical with *iso*phorone.

This method for preparing hydroaromatic ketones has been extended by using substituted malonic esters, but, unfortunately, the yields of the initial condensation products become smaller with increase in the molecular weight of the substituting group. Thus while it has been found possible to prepare *dimethylethyl*- and *dimethylpropyl*-cyclo*hexenones*, only traces of a condensation product could be isolated from the interaction of chlorodimethyl*cyclo*hexenone and ethyl *iso*propylmalonate, and the method would not, therefore, appear to be of any practical utility for the preparation of the higher members of the series.

***271. "Note on the determination of the rate of chemical change by measurement of the gases evolved." By John Cannell Cain and Frank Nicoll.**

The authors showed that the criticism of their work on the rate of decomposition of diazobenzene chloride, advanced by F. E. E. Lamplough in a paper bearing the above title and read before the Society in 1906 (*Proc.*, **22**, 280; compare also *Proc.*, 1908, **24**, 29) and recently published in full (*Proc. Camb. Phil. Soc.*, 1908, **14**, 580), are invalid for the following reasons: (1) It is definitely stated in their paper (*Trans.*, 1902, **81**, 1415) that "the flask usually contained pieces of broken glass for purposes of adjustment, and was well shaken during this operation (of heating the diazo-solution to the required temperature) to avoid overheating," and hence supersaturation was impossible. (2) The whole of the calculated amount of nitrogen was measured; hence none was retained by the solution beyond the minimum quantity (which is within the limits of experimental error) ordinarily dissolved.

Moreover, it was pointed out that Lamplough has overlooked Euler's proof that the reaction is accelerated by colloidal platinum, for in the experiments on the decomposition of hydrogen peroxide the platinum stirrer was coated with wax to guard against any possible action of the platinum, whilst this precaution was omitted in the experiments on diazobenzene chloride. This may well account for the higher value of the constants obtained. Further, Euler has proved by experiment that no supersaturation of the solution with nitrogen takes place in the decomposition of the diazo-solution (*Annalen*, 1902, **325**, 295). Finally, the authors expressed the opinion that Lamplough's method of measuring the value of constants which vary enormously with the temperature (being multiplied three to four times for a difference of 10°), by omitting to carry out his experiments with a thermometer in the reacting liquid, and by heating the diazo-solution "one or two degrees higher than (the temperature of) the water-bath," which again would raise the value of the constant found, cannot be regarded as an exact one, and the conclusion was drawn that the authors' determinations of the values of the constants in question (in which the temperature was carefully maintained at the correct point) are to be looked upon as being the most accurate yet recorded.

Discussion.

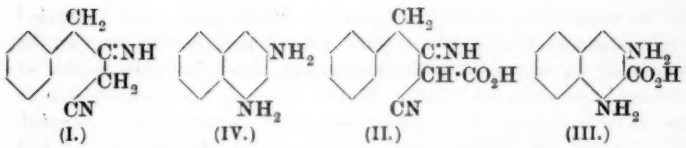
Dr. Senter said he did not think that Dr. Cain's solution could have been appreciably supersaturated under the conditions of experiment.

In his experience, however, solutions in which gases were generated might become highly supersaturated under certain conditions. In the course of an attempt to determine the rate of decomposition of hydrogen peroxide by highly diluted blood (1 of blood to 500 of water) by measuring the oxygen liberated (compare *Zeitsch. physikal. Chem.*, 1903, **44**, 257), it was found that if the reaction was allowed to proceed quietly for some time, and the bottle was then vigorously shaken, an immediate increase in the volume of the oxygen, amounting to several c.c., was observed, although, as shown by subsequent investigation, the course of the reaction is perfectly regular. The amount of oxygen held in solution before shaking amounted at least to five times the ordinary solubility of the gas, and could not be due to chemical combination with the constituents of the blood (1) because of the exceedingly small proportion of blood present (under ordinary conditions blood only takes up about 20 per cent. of its volume of oxygen at atmospheric pressure); (2) because the gas was set free by shaking alone.

The PRESIDENT remarked that certain colloidal and albuminous substances have a considerable influence in causing their solutions to retain gas in solution: he alluded to the solubility of nitrogen in blood-serum. He understood from Dr. Senter that the subject is being investigated by Dr. Findlay.

272. "The formation and reactions of imino-compounds. Part VII. The formation of 1:3-naphthylenediamine from β-imino-α-cyano-γ-phenylpropane." By Stanley Robert Best and Jocelyn Field Thorpe.

In order to study the effect of concentrated sulphuric acid on benzenoid imino-nitriles containing no other substituting groups in the side-chain, attempts were made to prepare *β-imino-α-cyano-γ-phenylpropane* (I) by the condensation of phenylacetonitrile with acetonitrile, but without success. It was ultimately found that this substance can be prepared by the action of alcoholic sodium ethoxide on ethyl β-imino-α-cyano-γ-phenylbutyrate, $CH_2Ph{\cdot}C(:NH){\cdot}CH(CN){\cdot}CO_2Et$, which yields, in the first instance, *β-imino-α-cyano-γ-phenylbutyric acid* (II), and subsequently, by the elimination of carbon dioxide, the above imino-nitrile. Both β-imino-α-cyano-γ-phenylbutyric acid and β-imino-α-cyano-γ-phenylpropane pass into naphthalene derivatives on treatment with concentrated sulphuric acid, the former into 1:3-naphthylenediamine-2-carboxylic acid (III) and the latter into 1:3-naphthylenediamine (IV):



(I.) (IV.) (II.) (III.)

During the experiments on the conditions of hydrolysis of ethyl β-imino-α-cyano-γ-phenylbutyrate with one equivalent of alcoholic potash, it was found that when methyl alcohol is the solvent used the ethyl salt is completely converted into *methyl β-imino-α-cyano-γ-phenylbutyrate*, $CH_2Ph{\cdot}C(:NH){\cdot}CH(CN){\cdot}CO_2Me$, and that when water is present the potassium compound of methyl α-cyano-γ-phenylacetoacetate, $CH_2Ph{\cdot}CO{\cdot}CK(CN){\cdot}CO_2Me$, is the sole product. Methyl β-imino-α-cyano-γ-phenylbutyrate passes into *methyl* 1 : 3-*naphthylenediamine*-2-*carboxylate* on treatment with sulphuric acid.

273. "The absorption spectra of para-benzoquinone, quinol, and quinhydrone in the state of vapour and in solution." By Walter Noel Hartley and Alfred Godfrey Gordon Leonard.

The absorption spectra of *p*-benzoquinone and various derivatives in solution were examined by Hartley, Dobbie, and Lauder (*Brit. Assoc. Rep.*, 1902, p. 107), and compared with the various structural formulæ which had been proposed for these substances. The chemical reactions of *p*-benzoquinone were referred to, particularly its powerful oxidising action on alcohols (Ciamician and Silber, *Ber.*, 1901, **34**, 1350), and therefore alcohol had been regarded as an unsuitable solvent. Baly and Stewart (*Trans.*, 1906, **89**, 506) regard water as an unsatisfactory solvent and employ alcohol. They find the curve for *p*-benzoquinone in alcoholic solution to be quite different from that observed by Hartley, Dobbie, and Lauder. Experiments made by one of the present authors, in 1902, seemed to show that both alcoholic and aqueous solutions under the action of light yield quinol, and the band of quinol is indicated on the curves. To ascertain the absorption spectrum of pure *p*-benzoquinone, photographs of the absorption spectrum of its vapour which had been already obtained were compared with those of a solution of the substance in a neutral solvent, such as ether. The results led to an extension of the work to quinol and quinhydrone, in consequence of the discovery of a reversible reaction, expressed in terms of the following equation: $C_6H_6O_2 \rightleftarrows C_6H_4O_2 + H_2$, when quinol vapour is heated in air to 147° at atmospheric pressures and exposed to light. When heated in hydrogen, the quantity of *p*-benzoquinone produced is diminished.

Among the conclusions arrived at are, that ether is the only suitable solvent at all concentrations, and that under the influence of sunlight, or ultra-violet rays, an interaction occurs between the solvent alcohol and the solute *p*-benzoquinone which leads to the reduction of the latter to quinol or quinhydrone.

274. "The constitution of para-benzoquinone." By Walter Noel Hartley.

In a previous paper, the author has shown how the formula for benzene as proposed by Kekulé might be reconciled with those of Armstrong and von Baeyer (*Trans.*, 1905, **87**, 1823). From the evidence obtained during the investigation of *p*-benzoquinone, and of benzene and its homologues in a state of vapour (*Phil. Trans.*, 1908, *A*, **208**, 475), it now appears certain that neither *p*-benzoquinone nor quinol has a fixed and settled constitution in the strict sense of their usual symbolic representations, or the interpretations of them. It has been proved that *p*-benzoquinone is a benzene derivative, and furthermore, that it is possessed of a dual character in the sense that the function of the molecule can be either that of a double ketone or of a peroxide, according to circumstances. The reversible reaction described in the previous paper by Mr. Leonard and the author is now under further investigation.

275. "Benzyl sulphoxide: a possible example of dynamic isomerism." By John Armstrong Smythe.

By the action of hydrochloric acid on benzyl sulphoxide, four to six of the following compounds are produced: benzaldehyde, benzyl chloride, benzyl mercaptan, benzyl disulphide, benzyl sulphide, benzyl disulphoxide, and benzaldehyde benzylmercaptale. The study of this reaction under different conditions has shown that it is influenced by temperature, and the nature of the solvent in which it takes place; the oxygen of the sulphoxide passes over chiefly into the disulphoxide in aqueous solvents, but progressively larger amounts of benzaldehyde are formed as the solvent becomes more anhydrous and the temperature rises.

To account for these and allied phenomena, it is assumed that benzyl sulphoxide exists in solution in two forms, which differ constitutionally in the position of the oxygen atom in the molecule. On the basis of this hypothesis, a series of equations involving the tautomeric forms is proposed, which gives a simple and consistent account of the formation

of all the various products, and enables the hypothesis to be tested by comparison of the quantities calculated from the equations with those found experimentally. The agreement of calculated with experimental results is held to justify the hypothesis.

The quantitative data enable further the equilibrium between the tautomerides under certain conditions to be investigated, and they also show the influence of water as catalyst in the conversion of one form into the other.

Confirmatory evidence of these views is obtained from other reactions of benzyl sulphoxide.

276. "The chemical dynamics of the reactions between sodium thiosulphate and organic halogen compounds. Part III." By Arthur Slator and Douglas Frank Twiss.

The velocities of the reactions between sodium thiosulphate and the following halogen compounds have been measured: propyl iodide, *iso*propyl iodide, allyl iodide, chloroacetone, chloroacetophenone, benzyl chloride, *o*-, *p*-, and *m*-nitrobenzyl chlorides, ethyl α-bromopropionate, and ethyl α-bromobutyrate. The great activity of the acetone derivatives is remarkable. Allyl iodide is more reactive than methyl iodide. The activity of the benzyl chlorides is of the same order of magnitude as that of methyl chloride. The *iso*-compounds are less reactive than the corresponding normal compounds.

To explain to a certain extent the results of this and other investigations, it is suggested that the halides exist in more than one form in solution, and that some reagents react with one form and some with another.

277. "Note on the optical rotatory power of menthyl cinnamate." By Thomas Percy Hilditch.

The author's observations on menthyl cinnamate (*Trans.*, 1908, **93**, 1) showed that his specimen of this ester, although identical in most physical properties with those described by Tschugaeff (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 606) and Cohen and Whiteley (*Trans.*, 1901, **79**, 1308), possessed in chloroform solution a widely different rotation from that given by Tschugaeff for the liquid ester ($[\alpha]_D$ – 86·65°).

An opportunity for further investigation of this point has been afforded by experiments made primarily with the view of ascertaining the degree of accuracy of a polarimeter in the University of Jena; two samples of menthyl cinnamate were prepared, one from cinnamic

acid procured from Kahlbaum, and the other from acid prepared by the author from benzaldehyde by Perkin's reaction. The menthol possessed a specific rotation $[\alpha]_D^{15}$ $-48{\cdot}84°$ in 5 per cent. chloroform solution. The purification of the esters was accomplished, as previously, by two successive distillations in a vacuum; the boiling point of each sample was 210—212°/20 mm.

In 10 per cent. chloroform solution the first preparation had $[\alpha]_D^{15}$ $-60{\cdot}44°$, and the second $[\alpha]_D^{15}$ $-60{\cdot}50°$; the value previously obtained with menthol, $[\alpha]_D^{20}$ $-48{\cdot}40°$, was $[\alpha]_D^{20}$ $-60{\cdot}00°$. On examining the compound without a solvent, however, the observed optical activity was $[\alpha]_D^{15}$ $-85{\cdot}95°$.

It was obviously a matter of great difficulty to determine, at the temperature of the experiments, the molecular condition of the ester, either undissolved or dissolved in chloroform. The rotatory power in glacial acetic acid was therefore measured, when a 5 per cent. solution gave $[\alpha]_D^{15}$ $-60{\cdot}02°$. It may thus be assumed that the molecular state of the substance here is the same as in chloroform. A molecular-weight determination by the freezing-point method in glacial acetic acid solution showed the ester to be unimolecular (0·2204 ester in 26·804 acetic acid gave $\Delta = 0{\cdot}113°$, whence M.W. = 280·8. $C_{19}H_{26}O_2 = 286$); hence the substance is unimolecular in acetic acid and also in chloroform solution, whilst in the undissolved state it is probably associated. It may be noted that the corresponding menthyl β-phenylpropionate possesses the same rotatory power in the fused state as in chloroform solution.

Similar irregularities have been mentioned by Rupe (*Annalen*, 1903, **327**, 164) in the case of menthyl acetate, which possesses less activity in alcohol solution than when no solvent is used, although all the other menthyl fatty acid esters show greater optical activity in alcohol than in the absence of solvent, and by Freundler (*Compt. rend.*, 1893, **117**, 556; *Ann. chim. phys.*, 1895, [vii], **4**, 244), who showed that ethyl alcohol, methyl alcohol, and acetone solutions of dipropyl diacetyl-tartrate have a weaker rotatory power than the undissolved substance, whilst dipropyl dibutyryl- and dihexyl-tartrates possess stronger activity in these solvents than in the undissolved state.

It follows from the above results that such esters are not in the same molecular condition when undissolved as when in solution, and that any measurements designed for the purpose of comparing the rotatory powers of a series of substances should be conducted in circumstances which ensure that the compounds in question are present in a normal, or, in other words, unimolecular, condition.

278. "Liberation of iodine from hydriodic acid by certain halogenated malonyl derivatives." By Martha Annie Whiteley.

During the continuation of the work on derivatives of malonamide (*Proc.*, 1904, **20**, 92) and of barbituric acid (*Trans.*, 1907, **91**, 1330), it has been observed that the mono- and dibromo-derivatives of these series, compounds containing the complex $-CO\cdot CHBr\cdot CO-$ or $-CO\cdot CBr_2\cdot CO-$,

liberate iodine from hydriodic acid at the ordinary temperature according to the equation $>CBr_2 + 4HI = >CH_2 + 2HBr + 2I_2$.

In most cases the reaction is complete, and can be employed as a method for estimating the bromine in the compounds. Quantitative results have been obtained with dibromomalonamide, *bromomalonyldiurethane*, $(CO\cdot NH\cdot CO_2Et)_2CHBr$, m. p. 148°, 5 : 5-dibromo-1 : 3-diphenylbarbituric acid, *5-bromo-5-benzoyl-1 : 3-diphenylbarbituric acid*, $C_{23}H_{15}O_4N_2Br$, m. p. 186°, *5-bromo-1 : 3-diphenyl-2-thiobarbituric acid*, $CS<^{NPh\cdot CO}_{NPh\cdot CO}>CHBr$, m. p. 220°, and *5 : 5-dibromo-1 : 3-diphenyl-2-thiobarbituric acid*, $CS<^{NPh\cdot CO}_{NPh\cdot CO}>CBr_2$, m. p. 190°; and some of these compounds react also with silver nitrate in the presence of dilute nitric acid, forming silver bromide.

Dichloromalonamide slowly liberates iodine from hydriodic acid at the ordinary temperature, but the reaction is not complete even at 100°.

The replaceability of halogen by hydrogen by the action of hydriodic acid at the ordinary temperature has hitherto been regarded as a characteristic reaction of compounds containing the nitrogen-halogen as distinguished from those containing the carbon-halogen linking (Chattaway, *Trans.*, 1905, **87**, 145; *Chem. News*, 1908, **98**, 285); since the results quoted above show that this generalisation is no longer tenable, it seemed advisable to publish this preliminary statement. The investigation is being extended to other compounds containing the $>CHX$ or $>CX_2$ group to ascertain to what extent the replaceability of the halogen is influenced by the nature of the neighbouring groups.

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Continued from vol. xi as—

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[*The words "und Pharmacie" were dropped in* 1874.]

—— Supplement Band. Vols. i—viii. Leipzig 1861—1872.

—— General register.. Vols. i—cclxxvi. 5 vols. Leipzig 1843—1895.

Annales de Chimie et de Physique. 2nd series. By **Gay-Lussac** and **Arago.** [after vol. lxxiii] by **Gay-Lussac, Arago, Chevreul, Savary, Dumas, Pelouze, Boussingault,** and **Regnault.** 75 vols. Paris 1816—40. [Vols. i—iii, reprinted. Paris 1830.]

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—— 4th series. By **Chevreul, Dumas, Pelouze, Boussingault,** and **Regnault,** avec la collaboration de **Wurtz,** [*after* vol. xv] by **Chevreul, Dumas, Boussingault, Regnault,** and **Wurtz,** avec la collaboration de *M.* **Bertin.** 30 vols. Paris 1864—73.

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—— Tables des matières. Series II. 3 vols. Paris 1831—1841. Series VI. Paris 1895.

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—— **The Journal of the Chemical Society.** New series. Vol. i, 1863, etc. [Whole series, Vol. xvi, etc.] Vols. xvi—xxxii, edited by *H.* **Watts.** Vols. xxxiii—xlvi, edited by *H.* **Watts** and *C. E.* **Groves.** Vols. xlvii—lxxiv, edited by *C. E.* **Groves** and *A. J.* **Greenaway.** Vols. lxxv—lxxvi, edited by *C. E.* **Groves,** *W. P.* **Wynne,** and *A. J.* **Greenaway.** Vols. lxxvii—lxxxii, edited by *W. P.* **Wynne** and *A. J.* **Greenaway.** Vols. lxxxiii—lxxxviii, edited by *G. T.* **Morgan** and *A. J.* **Greenaway.** Vols. lxxxix—xc, edited by *G. T.* **Morgan,** *J. C.* **Cain,** *A. J.* **Greenaway,** and *C. H.* **Desch.** Vol. xci, etc., edited by *J. C.* **Cain,** *A. J.* **Greenaway,** and *C. H.* **Desch.** London 1863, etc.

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and Proceedings (1841—47). Compiled by *H.* **Watts**. London 1874.

A collective index of the Transactions and Abstracts of the Chemical Society, 1873—82. Compiled by *Margaret D.* **Dougal**. London [1899].

—— A collective index of the Transactions, Proceedings, and Abstracts of the Chemical Society, 1833—92. Compiled by *M. D.* **Dougal**. Part I. Index of Authors. Part II. Index of Subjects. 2 vols. London [1898].

—— A collective index of the Transactions . . . Compiled by *M. D.* **Dougal**. 1893—1902. 2 vols. London [1904—5].

Deutsche chemische Gesellschaft, Berlin. Berichte. Vol. i. 1868, etc. From vol. vi, 1873—82, edited by *H.* **Wichelhaus**; 1883—85, edited by *F.* **Tiemann**; 1886—96, edited by *F.* **Tiemann** and *F. von* **Dechend**; 1897—98, edited by *F.* **Tiemann** and *P.* **Jacobson**; 1898, etc., edited by *P.* **Jacobson**. Berlin 1868+.

—— General register. 1868—77. Edited by *C.* **Bischoff**. Berlin 1880.

—— General register. 1878—87. By *F.* **Tiemann** and *F. von* **Dechend**. Berlin 1888.

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At the next Ordinary Meeting on **Thursday**, January **21st**, 1909, at **8.30** p.m., the following papers will be communicated:

"Organic derivatives of silicon. Part IX. Experiments on the resolution of *dl*-benzylethylpropyl*iso*butylsilicane sulphonic acid." By F. S. Kipping and (in part) H. Davies.

"Synthesis of diurea from urea." By F. D. Chattaway.

"Chlorine derivatives of substituted ureas." By F. D. Chattaway and D. F. S. Wünsch.

"Chemical examination of eriodictyon. Part II." By F. Tutin and H. W. B. Clewer.

"The hydration of precipitates." By S. P. U. Pickering.

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